

# Smoluchowski Dynamics and the Ergodic-Nonergodic Transition

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## Abstract

We use the recently introduced theory for the kinetics of systems of classical particles to investigate systems driven by Smoluchowski dynamics. We investigate the existence of ergodic-nonergodic (ENE) transitions near the liquid-glass transition. We develop a self-consistent perturbation theory in terms of an effective two-body potential and work to second order in this potential. At second order, we have an explicit relationship between the static structure factor and the effective potential and choose the static structure factor in the case of hard spheres to be given by the solution of the Percus-Yevick approximation for hard spheres. Then, using the analytically determined ENE equation for the ergodicity function, we find an ENE transition for packing fraction  $\eta$  greater than a critical value  $\eta^* = 0.76$  which is physically inaccessible. The existence of a linear fluctuation-dissipation theorem in the problem is shown and used to great advantage.

## I. INTRODUCTION

We continue<sup>1</sup> our presentation of a self-consistent approach to the kinetics of classical systems of particles by studying the fluctuations in equilibrium of a system driven by Smoluchowski dynamics. We first show that the system obeys a linear fluctuation-dissipation theorem (FDT). This simplifies the structure of the theory significantly giving the conventional linear relation between the density-density correlation function and the conjugate response function. We present here a perturbation theory valid to second order in an effective interaction potential. Because of the self-consistency we are able to show that this expansion is useful even for systems with hard-core interactions.

This approach was demonstrated at first order in Ref. 1 (henceforth referred to as FTSPD) where the effective potential is found to be proportional to the direct correlation function. Here we extend the calculation to second order. In this paper we focus on the collective (or Ornstein-Zernike) second order self-energies. We show that these self-energies are quadratic functionals of the full density-density correlation functions, the components of the self-energies individually satisfy a FDT, no wave-number or frequency cut offs are needed<sup>2</sup>, and the set of Dyson equations fundamental to the theory can be replaced by a single-kinetic equation of the same form as that produced in memory-function theories<sup>3,4</sup>.

Going further, one can show that the collective contribution, again using the FDT, gives a relation for the static structure which agrees with the result from a purely static calculation giving the structure factor in terms of the direct correlation function and the direct correlation function self-consistently in terms of the static structure factor. Our approach is to assume the static structure factor is known and to solve for that effective potential which satisfies the second order structural equation. This effective potential is then available in the dynamical calculations. It could also be used in other static calculations. We focus here primarily on the large wavenumber regime near the structure factor maximum.

We also show that it is only the collective part of the self-energy which enters into the determination of the ergodic-nonergodic (ENE) phase-diagram. The ENE transition occurs when the density-density correlation develops a zero-frequency  $\delta$  function. The amplitude of this  $\delta$  function satisfies a nonergodicity equation. This equation is very similar to that found<sup>5</sup> in mode-coupling theory (MCT). For a system characterized by a structure factor obtained as the solution of the Percus-Yevick approximation<sup>6</sup> for hard-spheres we find a transition

at packing fraction  $\eta^* = 0.76$ . Conventional MCT gives  $\eta = 0.51$ . As obtained here,  $\eta^*$  is well above any physically attainable density in agreement with experiment and simulation. If we drop self-consistency and use the first order effective potential in determining  $\eta^*$  we obtain the value  $\eta^* = 0.60$  even though the first and second order effective potentials are very similar. Therefore  $\eta^*$  is a rather sensitive quantity. Despite our prejudices that there is no physical ENE transition in the single-component hard-sphere Smoluchowski dynamics, more work checking perturbations to our solution is required before one can claim a “proof” of the lack of a transition.

Experience guides us to be skeptical<sup>7</sup> about the stability of this transition under the inclusion of higher order terms in perturbation theory. Happily one can test this skepticism by going to higher order in the expansion. This appears to be technically feasible.

In a companion paper we discuss the *single-particle* contribution to the second order self energies. This term in the second order self-energy makes no contribution to the structural statics (static structure factor) but does involve the equation of state. It also does not come into the nonergodicity-equation determining the ENE phase diagram. This does not mean that it plays no role in the slow dynamics of the system. Quite to the contrary, this term depends linearly on  $G_{\rho\rho}$  and in a way which suggests the  $F_{12}$  model of Goetze<sup>8</sup> and a mechanism for stretching the dynamics.

We find that the self-energy  $\Gamma_{BB}$  is a functional, to arbitrary order in the effective potential, of the full-density-density correlation function. Setting aside the difficult question of vertex renormalization, the construction of  $\Gamma_{BB}$  to arbitrary order appears feasible. This involves construction of the self-energy  $\Gamma_{BB}$  as a polynomial in  $G_{\rho\rho}$  which produces a zero-frequency  $\delta$  function in response to the a zero-frequency  $\delta$  function developing in  $G_{\rho\rho}$  in the nonergodic state.

We are interested in the kinetics of colloidal suspensions. They are of interest because one can apparently carry out clean experiments in the regime where the system becomes glassy or crystallizes<sup>9</sup>. The system is also of interest because the colloidal particles are buffeted by a bath of smaller particles which has the effect of rapidly thermalizing the momentum degrees of freedom. This process is carefully described by Fokker-Planck (FP) dynamics. In FP dynamics the Newtonian equations of motion are supplemented by noise terms. It is very convenient to study a simpler dynamics than Fokker-Planck or Newtonian dynamics<sup>10</sup>. To a first approximation in colloids we can assume that the momenta thermalize quicker than the

position variables. Smoluchowski dynamics<sup>11</sup> assumes that the momenta are thermalized and particles move via a random walk or diffusion process interacting with the same two-body forces as in the Newtonian case. In the noninteracting limit one has  $N$ -Brownian<sup>12</sup> particles.

While the Smoluchowski dynamics offer a complete self-consistent dynamical system with a static structure equivalent to that for Newtonian and FP dynamics, there has been a search for simpler, coarse-grained field theories applicable to the colloidal system. Considerable energy has been focused on the Dean-Kawasaki (SDK) model<sup>13,14</sup>. The MSR action for this model<sup>15</sup> is given by

$$A_{DK} = \int d1 \left[ D\rho(\nabla\hat{\rho})^2 + i\hat{\rho} \left[ \frac{\partial\rho}{\partial t} - \nabla\left(\rho\nabla\frac{\delta F}{\delta\rho}\right) \right] \right] \quad (1)$$

where  $\rho$  is a density continuous field and  $\hat{\rho}$  is its response conjugate. The functional derivative of the effective free energy, taken from density functional theory, is given by

$$\frac{\delta F}{\delta\rho(x)} = T \ln \rho(x) + \int d^d y \, u(x-y) \delta\rho(y) \quad (2)$$

where the ideal gas contribution is proportional to  $\ln \rho$  and  $u$  is related to the direct correlation function. An apparently appealing feature of this model is that the ideal-gas contribution to the equation of motion satisfies

$$\nabla\left(\rho\nabla\frac{\delta F_{IDG}}{\delta\rho}\right) = T\nabla^2\rho. \quad (3)$$

There has been considerable effort to study the SDK system<sup>2</sup>. The most complete analysis is due to Kim and Kawasaki<sup>16</sup>. Analysis of the SDK model field theory uncovers multiple complications such as nonpolynomial nonlinear structure and multiplicative noise structure. This leads to an impractical nonlinear form of FDT relating response and correlation functions. In the end, one is not definitively able to answer the question: Is there an ENE transition at one-loop order for the SDK model?

Our second order self-consistent microscopic theory suffers none of these problems and gives a definitive answer to the ENE transition question. An interesting point is how the theory handles convergence of integrals in perturbation theory. The theory naturally organizes itself into a structure with self-dressed propagators. This leads to convergent integrals in perturbation theory. One finds that self-dressed propagators occur order to order in perturbation theory. The dressing consists in multiplication of the physical correlation function

by factors of  $G^{(0)}$  and the effective potential. It is crucial that one recognize that these self-dressed correlation functions themselves satisfy a FDT.

It is extremely useful that the linear FDT holds in the theory. This facilitates the use of a simple kinetic equation in treating the time evolution and separating out the static behavior.

While not immediately apparent, the understanding of the role of one-particle irreducible vertex functions in this analysis is very important. The expansion parameter is not, as in conventional field theory, in terms of the vertices. There are nonzero nonlinear vertices even at zeroth order in the interaction. An example is the cubic 1PI vertex. The one-particle irreducible vertices are interesting even in the noninteracting limit. Starting at the four-point vertices one must deal with one-particle reducible contributions to the cumulant structure. Vertices are now generally frequency dependent. We reserve the discussion of the four-point vertices to the next paper in this series.

The static theory can be developed in complete analogy with the dynamic theory. In particular one can work out the self-consistent static expansion in terms of the effective potential. One finds exactly the same results for the statics using dynamics and statics.

The approach taken here is fully microscopic and allows one to calculate in detail. This is in contrast with the projection operator technique which allows one to develop a useful phenomenological description of a problem. There was a substantial effort<sup>17</sup> to show that a noninteracting Brownian gas can be described by a nontrivial but solvable cubic MSR field theory. Our work has been compatible with these results finding agreement for the set of Brownian-density cumulants.

## II. SMOLUCHOWSKI DYNAMICS

Let us begin by defining the dynamical system of interest. Consider a set of  $N$  particles with configurations specified by the coordinates  $R_i$  which satisfy the equations of motion

$$\dot{R}_i = DF_i + \eta_i \quad (4)$$

where the particles experience force

$$F_i = -\frac{\partial}{\partial R_i} U(R), \quad (5)$$

with total potential

$$U(R) = \frac{1}{2} \sum_{i \neq j} \bar{V}(R_i - R_j) \quad (6)$$

where  $\bar{V}$  is a pair potential. There is a noise source  $\eta_i$  for each coordinate which is taken to be Gaussian with variance

$$\langle \eta_i(t) \eta_j(t') \rangle = 2k_B T D \delta(t - t') \delta_{ij} \quad (7)$$

where  $D$  is a diffusion coefficient.

We showed in FTSPD that one can set up a useful self-consistent perturbation theory if we develop the theory in terms a small set of collective variables  $\Phi$ . For this system, the density  $\rho$  is essential since it governs the static equilibrium behavior and, from the point of view developed here, is always included in  $\Phi = (\rho, \dots)$ . The set  $\Phi$  must also include a response field  $B$  (described below) if we are to control and manipulate the interactions in the system. The set of collective variables treated [ $\Phi = (\rho, B, \dots)$ ], is flexible and controlled by pairing each observable with a conjugate external field [ $H = (H_\rho, H_B, \dots)$ ] Here we specifically treat fluctuations in equilibrium and choose [ $\Phi = (\rho, B)$ ]. We assume the system is in equilibrium initially [ $t = t_0$ ,  $R_i(t_0) = R_i^{(0)}$ ] and the initial distribution for a set of  $N$  particles is canonical:

$$P_0[R^0] = e^{-\beta U(R^{(0)})} / Z_0 \quad (8)$$

where  $U$  is the potential energy defined by Eq.(6) and  $\beta$  is the inverse temperature. The MSR action for the problem is given by

$$A_R = \int_{t_0}^{\infty} dt_1 \sum_{i=1}^N \left[ \hat{R}_i(t_1) k_B T D \hat{R}_i(t_1) + i \hat{R}_i(t_1) \cdot (\dot{R}_i(t_1) - D F_i(t_1)) \right] + A_J \quad (9)$$

where the contribution to the action  $A_J$  is from the notorious Jacobian<sup>18</sup>.

It was shown in FTSPD that this action can be written in the highly compact form

$$A = A_0 + A_I \quad (10)$$

where  $A_0$  is the quadratic part of the action excluding the quadratic contribution to the initial probability distribution,

$$A_0 = \int_{t_0}^{\infty} dt_1 \sum_{i=1}^N \left[ \hat{R}_i \bar{D} \hat{R}_i + i \hat{R}_i \cdot \dot{R}_i \right], \quad (11)$$

where  $\bar{D} = k_B T D$  and where the interaction is given by

$$A_I = \frac{1}{2} \sum_{\alpha, \nu} \int d1 d2 \Phi_\alpha(1) \sigma_{\alpha\nu}(12) \Phi_\nu(2). \quad (12)$$

The Greek labels range over  $\rho$  and  $B$  and we introduce the interaction matrix

$$\sigma_{\alpha\nu}(12) = -\beta V(12) \left[ \hat{\rho}_\alpha \hat{\rho}_\nu \delta(t_1 - t_0) - \beta^{-1} \left( \hat{\rho}_\alpha \hat{B}_\nu + \hat{B}_\alpha \hat{\rho}_\nu \right) \right] \quad (13)$$

where we have introduced the useful notation

$$\hat{\rho}_\alpha = \delta_{\alpha\rho}, \hat{B}_\alpha = \delta_{\alpha B} \quad (14)$$

and

$$\bar{V}(12) = \bar{V}(x_1 - x_2) \delta(t_1 - t_2). \quad (15)$$

The conjugate field is given by

$$B(1) = D \sum_{i=1}^N \left[ (\hat{R}_i i \nabla_1 + \theta(0) \nabla_1^2) \right] \delta(x_1 - R_i(t_1)). \quad (16)$$

The canonical partition function can be written in the convenient form

$$Z_N = \int \prod_{i=1}^N \left[ \mathcal{D}(R_i) \mathcal{D}(\hat{R}_i) d^d R_i^{(0)} \right] P_0(R_i^{(0)}) e^{-A_0 - A_I + H \cdot \Phi} \quad (17)$$

$$= Tr^{(N)} e^{-A_I + H \cdot \Phi}, \quad (18)$$

where we have introduced the average

$$Tr^{(N)} \mathcal{O} = \int \prod_{i=1}^N \left[ \mathcal{D}(R_i) \mathcal{D}(\hat{R}_i) d^d R_i^{(0)} \right] P_0(R_i^{(0)}) e^{-A_0} \mathcal{O}(R). \quad (19)$$

In the grand canonical ensemble,

$$Z_T[H] = \sum_{N=0}^{\infty} \frac{\rho_0^N}{N!} Tr^{(N)} e^{\int d1 H(1) \cdot \Phi(1)} e^{\frac{1}{2} \int d1 d2 \Phi(1) \cdot \sigma \cdot \Phi(2)}, \quad (20)$$

with the generator of cumulants given by

$$W[H] = \ln Z_T[H]. \quad (21)$$

### III. SELF-CONSISTENT DEVELOPMENT

It was shown in FTSPD that the one-point average

$$G_i = \langle \Phi_i \rangle = \frac{\delta}{\delta H_i} W[H] \quad (22)$$

satisfies the identity

$$G_i = \tilde{T} r \phi_i e^{H \cdot \phi + \Delta W[H]}, \quad (23)$$

where  $i$  labels space, time and fields  $\rho$  or  $B$ , and where

$$\Delta W[H] = W[H + F] - W[H] \quad (24)$$

with

$$F_i = \sum_j \sigma_{ij} \phi_j \quad (25)$$

and

$$\Phi_i = \sum_{\alpha=1}^N \phi_i^{(\alpha)}. \quad (26)$$

We have

$$\phi_\rho^{(0)}(1) = \delta[(x_1 - R^{(0)}(t_1))] \quad (27)$$

and

$$\phi_B^{(0)}(1) = D[\hat{R}^{(0)}(t_1) i \nabla_{x_1} + \theta(0) \nabla_{x_1}^2] \delta[x_1 - R^{(0)}(t_1)]. \quad (28)$$

These results were established in FTSPD using functional methods.

The dependence of the theory on the interaction potential is controlled by the quantity  $\Delta W[H] = W[H + F] - W[H]$ . We can expose the dependence on the potential by constructing the functional Taylor-series expansion

$$\Delta W[H] = \sum_i F_i \frac{\delta}{\delta H_i} W[H] + \sum_{ij} \frac{1}{2} F_i F_j \frac{\delta^2}{\delta H_i \delta H_j} W[H] + \dots \quad (29)$$

and we can conveniently introduce the set of cumulants

$$G_{ij\dots k} = \frac{\delta}{\delta H_i} \frac{\delta}{\delta H_j} \dots \frac{\delta}{\delta H_k} W[H] \quad (30)$$



to obtain

$$\Delta W[H] = \sum_i F_i G_i + \sum_{ij} \frac{1}{2} F_i F_j G_{ij} + \sum_{ijk} \frac{1}{3!} F_i F_j F_k G_{ijk} + \dots \quad (31)$$

with  $F_i$  given by Eq.(25). Clearly, in this form we can take  $\Delta W$  to be a functional of  $G_i$ . One can then use functional differentiation to express higher order cumulants in terms of the one- and two-point correlation functions  $G_i$  and  $G_{ij}$ .

Of particular interest is that we established in FTSPD a dynamic generalization of the static Ornstein-Zernike relation<sup>19</sup>. Taking the functional derivative of Eq.(23), we have

$$\begin{aligned} G_{ij} &= \frac{\delta}{\delta H_j} G_i \\ &= \mathcal{G}_{ij} + \sum_k c_{ik} G_{kj} \end{aligned} \quad (32)$$

where

$$\mathcal{G}_{ij} = \tilde{T}r \phi_i \phi_j e^{H \cdot \phi + \Delta W} \quad (33)$$

is a single-particle quantity and we have the memory function<sup>20</sup>, self-energy, or dynamic direct correlation function given by

$$c_{ij} = \tilde{T}r \phi_i e^{H \cdot \phi + \Delta W} \frac{\delta}{\delta G_j} \Delta W. \quad (34)$$

Since  $\Delta W$  can be treated as a functional of  $G_i$  we see at this stage that we have available a self-consistent theory. If we define the matrix inverses

$$\sum_k \Gamma_{ik} G_{kj} = \delta_{ij} \quad (35)$$

and

$$\sum_k \gamma_{ik} \mathcal{G}_{kj} = \delta_{ij} \quad (36)$$

then the two-point vertex is given without approximation as

$$\Gamma_{ij} = \gamma_{ij} + K_{ij}, \quad (37)$$

where

$$K_{ij} = - \sum_k \gamma_{ik} c_{kj} \quad (38)$$

is the collective contribution to the self-energy.

## IV. FLUCTUATION-DISSIPATION THEOREMS

### A. Introduction

The theory developed in FTSPD is very general and applicable to a wide variety of nonequilibrium problems. Here we look at fluctuations in equilibrium and see that one has a fluctuation-dissipation theorem (FDT) available. The existence of a FDT allows one to organize the theory very efficiently.

### B. Time-reversal symmetry

Let us focus on the time reversal transformation given by<sup>2</sup>

$$\tau R_i(t) = R_i(-t) \quad (39)$$

$$\tau \hat{R}_i(t) = -\hat{R}_i(-t) + i\beta F_i(-t). \quad (40)$$

How does the action

$$A = \int_{-\infty}^{\infty} dt \sum_i \left[ [\hat{R}_i(t) D\beta^{-1} \hat{R}_i(t)] + i\hat{R}_i(t) \left[ \frac{\partial}{\partial t} R_i(t) - DF_i(R) \right] \right] + A_J \quad (41)$$

change under the transformation? We have

$$\begin{aligned} A' &= \tau A \\ &= \int_{-\infty}^{\infty} dt \sum_i \left[ [-\hat{R}_i(-t) + i\beta F_i(-t)] D\beta^{-1} [-\hat{R}_i(-t) + i\beta F_i(-t)] \right. \\ &\quad \left. + i[-\hat{R}_i(-t) - i\beta F_i(-t)] \left[ \frac{\partial}{\partial t} R_i(-t) - DF_i(\tau R) \right] \right] + \tau A_J. \end{aligned} \quad (42)$$

We need to look at the various terms. Consider first

$$\begin{aligned} &\int_{-\infty}^{\infty} dt \sum_i \left[ -i\beta F_i(-t) \left[ \frac{\partial}{\partial t} R_i(-t) \right] \right] \\ &= \int_{-\infty}^{\infty} dt \sum_i (-i\beta)(-1) \frac{\delta U(-t)}{\delta R_i(-t)} i \frac{\partial}{\partial t} R_i(-t) \end{aligned}$$

$$= \int_{-\infty}^{\infty} dt \sum_i (-\beta) \frac{\partial}{\partial(-t)} U(-t) = \beta \int_{\infty}^{-\infty} ds \frac{\partial}{\partial s} U(s) = 0.$$

Next we collect the two force terms

$$\int_{-\infty}^{\infty} dt \sum_i \beta [(-1)F_i(-t)F_i(-t) + F_i(-t)F_i(-t)] = 0 \quad (43)$$

Putting this together we have

$$\begin{aligned} A' = \int_{-\infty}^{\infty} dt \sum_i & \left[ [-\hat{R}_i(-t)] D\beta^{-1} [-\hat{R}_i(-t) + 2i\beta F_i(-t)] \right. \\ & \left. + i[-\hat{R}_i(-t) \left[ \frac{\partial}{\partial t} R_i(-t) - DF_i(\tau R) \right]] \right] + \tau A_J \end{aligned} \quad (44)$$

where since  $A_J$  is a function of the density,  $\tau A_J = A_J$ . Then combining the terms linear in  $F$  and letting  $t \rightarrow -t$  we have the invariance principle  $A' = A$ .

### C. Application of the invariance principle to averages of fields

The first application of the invariance is to correlation functions. For the  $n$ -point density correlation function, we have, from its invariance under  $\tau$ ,

$$G_{\rho\rho\dots\rho}(1, 2, \dots, n) = G_{\rho\rho\dots\rho}(\tilde{1}, \tilde{2}, \dots, \tilde{n}) \quad (45)$$

where  $\tilde{\ell} = (x_\ell, -t_\ell)$ .

Consider the two-point response function

$$\begin{aligned} G_{\rho B}(12) &= \langle \rho(1) B(2) \rangle \\ &= \langle \rho(1) B_0(2) \rangle + \langle \rho(1) B_J(2) \rangle \end{aligned} \quad (46)$$

where the particle density is given by

$$\rho(1) = \sum_{i=1}^N \delta[x_1 - R_i(t_1)]. \quad (47)$$

The response field is the sum of

$$B_0(2) = D \sum_{i=1}^N i \hat{R}_i(t_2) \cdot \nabla_{x_2} \delta[x_2 - R_i(t_2)] \quad (48)$$

and

$$B_J(2) = \theta(0) D \nabla_{x_2}^2 \rho(2). \quad (49)$$

Applying  $\tau$  to  $B_0$

$$\begin{aligned} \tau B_0(2) &= D \sum_{i=1}^N [-\hat{R}_i(-t_2) + i\beta F_i(-t_2)] \cdot \nabla_{x_2} i\delta[x_2 - R_i(-t_2)] \\ &= -B_0(\tilde{2}) - \beta D \nabla_{x_2} F(\tilde{2}). \end{aligned} \quad (50)$$

We can then write  $\tilde{2} = (x_2, -t_2)$  and

$$\tau B(2) = -B(\tilde{2}) + 2B_J(\tilde{2}) - \beta D \nabla_{x_2} F(\tilde{2}). \quad (51)$$

Then we have on applying the invariance principle

$$G_{\rho B}(12) = -G_{\rho B}(\tilde{1}, \tilde{2}) + 2\theta(0) D \nabla_{x_2}^2 G_{\rho\rho}(\tilde{1}, \tilde{2}) - \beta D \nabla_{x_2} G_{\rho F}(\tilde{1}, \tilde{2}). \quad (52)$$

We now need an independent expression for the density-force density correlation function. As a first step construct an operator  $\hat{\mathcal{O}}_{B_0}(2)$  that satisfies

$$\hat{\mathcal{O}}_{B_0}(2) \int_{-\infty}^{\infty} dt \sum_{j=1}^N \hat{R}_j(t) \bar{D} \hat{R}_j(t) = B_0(2). \quad (53)$$

It is easy to see that

$$\hat{\mathcal{O}}_{B_0}(2) = \sum_{j=1}^N \frac{i\beta}{2} \nabla_{x_2} \cdot \frac{\delta}{\delta \hat{R}_j(t_2)} \delta[x_2 - R_j(t_2)]. \quad (54)$$

We now use the identity

$$Tr f(R) \hat{\mathcal{O}}_{B_0}(2) e^{-A} = 0 \quad (55)$$

or

$$\langle f(R) \hat{\mathcal{O}}_{B_0}(2) A \rangle = 0. \quad (56)$$

Letting the operator act on  $A$ , we have

$$\hat{\mathcal{O}}_{B_0}(2) A = B_0(2) - \frac{\beta}{2} \frac{\partial}{\partial t_2} \rho(2) + \frac{\beta D}{2} \nabla_{x_2} F(2) \quad (57)$$

$$= B(2) + \frac{\beta}{2} \left( \frac{-\partial}{\partial t_2} - \bar{D} \nabla_{x_2}^2 \right) \rho(2) + \frac{\beta D}{2} \nabla_{x_2} F(2). \quad (58)$$

Multiplying by the density and averaging, we have

$$\left\langle \rho(1) \left[ B(2) + \frac{\beta}{2} \left( \frac{-\partial}{\partial t_2} - \bar{D} \nabla_{x_2}^2 \right) \rho(2) + \frac{\beta D}{2} \nabla_{x_2} F(2) \right] \right\rangle = 0 \quad (59)$$

or

$$G_{\rho B}(12) + \frac{\beta}{2} \left( \frac{-\partial}{\partial t_2} - \bar{D} \nabla_{x_2}^2 \right) G_{\rho\rho}(12) + \frac{\beta}{2} \nabla_{x_2} G_{\rho F}(12) = 0. \quad (60)$$

Eliminating  $G_{\rho F}$  between Eqs.(52) and (60) we have

$$\begin{aligned} G_{\rho B}(12) &= -G_{\rho B}(\tilde{1}, \tilde{2}) + 2\theta(0) D \nabla_{x_2}^2 G_{\rho\rho}(\tilde{1}, \tilde{2}) + 2G_{\rho B}(\tilde{1}, \tilde{2}) \\ &\quad - \beta \left( \frac{\partial}{\partial t_2} + \bar{D} \nabla_{x_2}^2 \right) G_{\rho\rho}(\tilde{1}, \tilde{2}) \\ &= G_{\rho B}(\tilde{1}, \tilde{2}) - \beta \frac{\partial}{\partial t_2} G_{\rho\rho}(\tilde{1}, \tilde{2}). \end{aligned} \quad (61)$$

Since  $G_{\rho B}$  is retarded we can multiply by  $\theta(t_1 - t_2)$  and obtain the crucial FDT

$$\begin{aligned} G_{\rho B}(12) &= -\theta(t_1 - t_2) \beta \frac{\partial}{\partial t_2} G_{\rho\rho}(\tilde{1}, \tilde{2}) \\ &= \theta(t_1 - t_2) \beta \frac{\partial}{\partial t_1} G_{\rho\rho}(1, 2). \end{aligned} \quad (62)$$

#### D. FDT: Fourier Transform

The time Fourier transform of Eq.(62) is given by

$$\begin{aligned} G_{\rho B}(q, \omega) &= \int_{-\infty}^{\infty} dt e^{i\omega \cdot t} \beta \theta(t) \frac{\partial}{\partial t} G_{\rho\rho}(q, t) \\ &= \int_0^{\infty} dt e^{i\omega \cdot t} \beta \frac{\partial}{\partial t} \int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi} e^{-i\bar{\omega} t} G_{\rho\rho}(q, \bar{\omega}) \\ &= \int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi} (-i\bar{\omega}) G_{\rho\rho}(q, \bar{\omega}) \int_0^{\infty} dt e^{i(\omega \cdot -\bar{\omega})t} \end{aligned}$$

$$= \int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi} (-i\bar{\omega}) G_{\rho\rho}(q, \bar{\omega}) \frac{i}{\omega - \bar{\omega} + i\eta}. \quad (63)$$

So we have

$$G_{\rho B}(q, \omega) = \int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi} (\beta\bar{\omega}) \frac{G_{\rho\rho}(q, \bar{\omega})}{\omega - \bar{\omega} + i\eta}. \quad (64)$$

Taking the imaginary part

$$\begin{aligned} \text{Im } G_{\rho B}(q, \omega) &= \int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi} (\beta\bar{\omega}) \text{Im} \frac{G_{\rho\rho}(q, \bar{\omega})}{\omega - \bar{\omega} + i\eta} \\ &= -\frac{\beta\omega}{2} G_{\rho\rho}(q, \omega). \end{aligned} \quad (65)$$

It is useful to check the FDT in the noninteracting limit.

### E. FDT and vertex functions

Dyson's equation,

$$\sum_{\mu} \Gamma_{\alpha\mu} G_{\mu\beta} = \delta_{\alpha\beta}, \quad (66)$$

is a matrix equation relating matrix elements for the cumulants to the matrix elements of the vertex functions. Using  $G_{BB} = 0$  and  $\Gamma_{\rho\rho} = 0$  we have

$$G_{\rho B} = \frac{1}{\Gamma_{B\rho}}, \quad (67)$$

$$G_{B\rho} = \frac{1}{\Gamma_{\rho B}}, \quad (68)$$

and

$$G_{\rho\rho} = -\frac{1}{\Gamma_{B\rho}} \Gamma_{BB} \frac{1}{\Gamma_{\rho B}}. \quad (69)$$

Since  $G_{\rho B} = G_{B\rho}^*$  and  $\Gamma_{B\rho} = \Gamma_{\rho B}^*$ , we have

$$G_{\rho\rho} = -\frac{\Gamma_{BB}}{|\Gamma_{B\rho}|^2} \quad (70)$$

and since  $G_{\rho\rho}$  is positive, we have

$$\Gamma_{BB} < 0. \quad (71)$$

We can now use the FDT in the following way. Taking the imaginary part of  $G_{\rho B}$ ,

$$\begin{aligned} \text{Im } G_{\rho B} &= -\text{Im} \frac{\Gamma_{\rho B}}{|\Gamma_{B\rho}|^2} \\ &= -\frac{\beta\omega}{2} G_{\rho\rho}, \end{aligned} \quad (72)$$

and using Eq.(69) for  $G_{\rho\rho}$ , we can cancel the positive denominators and find

$$\text{Im } \Gamma_{\rho B} = \frac{\beta\omega}{2} \Gamma_{BB} \quad (73)$$

or

$$\text{Im } \Gamma_{B\rho} = -\frac{\beta\omega}{2} \Gamma_{BB}. \quad (74)$$

### F. Kinetic equation and the FDT

Starting with the  $B\rho$  component of Dyson's equation in  $q, t$  space, we have

$$\int d\bar{t} \Gamma_{B\rho}(q, t - \bar{t}) G_{\rho\rho}(q, \bar{t} - t') + \int d\bar{t} \Gamma_{BB}(q, t - \bar{t}) G_{B\rho}(\bar{t} - t') = 0. \quad (75)$$

Let us now write

$$\Gamma_{\alpha\beta}(q, t) = \gamma_{\alpha\beta}^{(1)}(q, t) - \Sigma_{\alpha\beta}(q, t) \quad (76)$$

where  $\gamma_{\alpha\beta}^{(1)}(q, t)$  includes the zeroth and first order contributions in perturbation theory and the self-energy  $\Sigma$  starts at second order. Suppressing the wavenumber label, we can rewrite Eq.(75) in the form

$$\gamma_{B\rho}^{(1)}(t) G_{\rho\rho}(t, t') + \gamma_{BB}^{(1)}(t) G_{B\rho}(t, t') = \Psi(t, t'), \quad (77)$$

where

$$\Psi(t, t') = \int_{-\infty}^t ds \Sigma_{B\rho}(t - s) G_{\rho\rho}(s - t') + \int_{-\infty}^{t'} ds \Sigma_{BB}(t - s) G_{B\rho}(s - t') \quad (78)$$

using the fact that  $\Sigma_{B\rho}(t - s) \sim \theta(t - s)$  and  $G_{B\rho}(s - t') \sim \theta(t' - s)$ . We then use the fluctuation-dissipation theorems

$$\Sigma_{B\rho}(t - s) = \theta(t - s) \beta \frac{\partial}{\partial t} \Sigma_{BB}(t - s) \quad (79)$$

$$G_{B\rho}(s - t') = \theta(t' - s)\beta\frac{\partial}{\partial t'}G_{\rho\rho}(t' - s) \quad (80)$$

to obtain

$$\Psi(t, t') = -\int_{-\infty}^t ds \left[ \beta\frac{\partial}{\partial s}\Sigma_{BB}(t - s) \right] G_{\rho\rho}(s - t') - \int_{-\infty}^{t'} ds \Sigma_{BB}(t - s)\beta\frac{\partial}{\partial s}G_{\rho\rho}(t' - s). \quad (81)$$

If we integrate the first integral by parts, we have

$$\begin{aligned} \Psi(t, t') &= -\beta\Sigma_{BB}(0)G_{\rho\rho}(t - t') + \beta\int_{-\infty}^t ds \Sigma_{BB}(t - s)\frac{\partial}{\partial s}G_{\rho\rho}(s - t') \\ &\quad - \int_{-\infty}^{t'} ds \Sigma_{BB}(t - s)\frac{\partial}{\partial s}G_{\rho\rho}(t' - s) \\ &= -\Sigma_{BB}(0)G_{\rho\rho}(t - t') + \int_{t'}^t ds \Sigma_{BB}(t - s)\frac{\partial}{\partial s}G_{\rho\rho}(t' - s) \end{aligned} \quad (82)$$

where we assume  $t > t'$ . We then have the kinetic equation

$$\beta\gamma_{B\rho}^{(1)}(t)G_{\rho\rho}(t, t') = -\beta^2\Sigma_{BB}(0)G_{\rho\rho}(t - t') + \beta^2\int_{t'}^t ds \Sigma_{BB}(t - s)\frac{\partial}{\partial s}G_{\rho\rho}(t' - s). \quad (83)$$

We see that our dynamical problem is now in the form of a memory function equation and the dynamic part of the memory function is given by the self-energy  $\Sigma_{BB}$ . With some additional work, one can show the equal-time quantity

$$\beta^2\rho_0\Sigma_{BB}(q, t = 0) = S^{-1}(q) - [1 + \rho_0\beta V(0)], \quad (84)$$

where  $V(q)$  is the Fourier transform of the potential. We will discuss these results in great detail elsewhere.

### G. Static Implications

The integral form of the FDT tells us that in the small  $\omega$  limit

$$G_{\rho B}(q, 0) = \int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi} (-\beta)G_{\rho\rho}(q, \bar{\omega}) \quad (85)$$

$$= -\beta S(q) \quad (86)$$

where  $S(q)$  is the static structure factor. One can also write this as

$$S(q) = -\frac{k_B T}{\Gamma_{B\rho}(q, 0)}. \quad (87)$$

This result will be extremely useful to us.



## V. IRREDUCIBLE VERTEX FUNCTIONS AND BROWNIAN GAS CUMULANTS

### A. Irreducible vertex functions

We list here the fundamental definitions relating the cumulants in the theory to the reducible vertex functions we need. The two-point irreducible vertex  $\Gamma_{ij}$  is defined by the Dyson's equation

$$\Gamma_{ik}G_{kj} = \delta_{ij}. \quad (88)$$

The three-point one-particle irreducible vertex is defined by

$$\Gamma_{ijk} = \frac{\delta\Gamma_{ij}}{\delta G_k} \quad (89)$$

which is equivalent to

$$G_{ijk} = \frac{\delta G_{ij}}{\delta H_k} = -G_{iu}G_{jv}G_{kw}\Gamma_{uvw} \quad (90)$$

which can be rewritten using Eq. (88) as

$$\Gamma_{ijk} = -\Gamma_{iu}\Gamma_{jv}\Gamma_{kw}G_{uvw}. \quad (91)$$

The case of four-point cumulants and irreducible vertex functions is discussed elsewhere<sup>22</sup>.

### B. Noninteracting Brownian particle cumulants: wavenumber and time regime

In FTSPD we derived a compact expression for the  $n$ -point cumulants for the fields  $\phi = (\rho, B)$ . In the time wavenumber regime, we have

$$G_{\alpha_1, \alpha_2, \dots, \alpha_n}^{(0)}(1, 2, \dots, n) = \rho_0 \delta(q_1 + q_2 + \dots + q_n) b_1 b_2 \dots b_n e^{N_n} \quad (92)$$

where  $b_j = b_{\alpha_j}(q_j, t_j)$  with

$$b_\rho(q_j, t_j) = 1, \quad (93)$$

$$b_B(q_j, t_j) = \beta \sum_{k=1 \neq j}^n K_{jk} \theta(t_k - t_j), \quad (94)$$

$$N_n = \frac{1}{2} \sum_{i,j=1}^n K_{ij} |t_i - t_j|, \quad (95)$$

and

$$K_{ij} = \bar{D} q_i \cdot q_j. \quad (96)$$

This expression is manifestly translationally invariant in space and time.

For our purposes, we need these cumulants Fourier transformed over time:

$$\begin{aligned} G_{\alpha_1, \alpha_2, \dots, \alpha_n}^{(0)}(1, 2, \dots, n) &= \rho_0 \delta(q_1 + q_2 + \dots + q_n) \\ &\times \int dt_1 dt_2 \dots dt_n b_1 b_2 \dots b_n e^{i \sum_{k=1}^n \omega_k t_k} e^{N_n}, \end{aligned} \quad (97)$$

where we have not found it confusing to use the same symbol for the Fourier transform. In this paper we assume the system is in an equilibrium state for all time.

### C. Time Fourier transform

We discuss the method of taking these time Fourier transforms elsewhere<sup>22</sup>. Here, we simply list the needed results. We will need the zeroth order two-point cumulants

$$G_{\rho\rho}^{(0)}(12) = 2\kappa_1 \rho_0 G_1 G_1^* \delta(1+2), \quad (98)$$

$$G_{B\rho}^{(0)}(12) = -\beta \kappa_1 \rho_0 G_1^* \delta(1+2), \quad (99)$$

$$G_{\rho B}^{(0)}(12) = -\beta \kappa_1 \rho_0 G_1 \delta(1+2), \quad (100)$$

and

$$G_{BB}^{(0)}(12) = 0, \quad (101)$$

where

$$\kappa_i = K_{ii} = \bar{D} q_i^2, \quad (102)$$

$$G_i^{-1} = -i\omega_i + \kappa_i, \quad (103)$$

and

$$\delta(1+2) = (2\pi)^d \delta(q_1 + q_2) 2\pi \delta(\omega_1 + \omega_2). \quad (104)$$

### D. Two-point vertices

We also need the zeroth order two-point irreducible vertices defined by

$$\gamma_{ik}^{(0)} G_{kj}^{(0)} = \delta_{ij}. \quad (105)$$

We find

$$\beta \gamma_{\rho\rho}^{(0)}(12) = 0, \quad (106)$$

$$\beta \gamma_{B\rho}^{(0)}(12) = -\frac{G_1^{-1}}{\rho_0 \kappa_1} \delta(1+2), \quad (107)$$

$$\beta \gamma_{\rho B}^{(0)}(12) = -\frac{G_1^{-1,*}}{\rho_0 \kappa_1} \delta(1+2), \quad (108)$$

and

$$\beta^2 \gamma_{BB}^{(0)}(12) = -\frac{2}{\rho_0 \kappa_1} \delta(1+2). \quad (109)$$

These are the key building blocks of the theory.

### E. Three-point vertices

A key role in the second order theory is played by the zeroth order three-point irreducible vertices. These are defined in terms of the three-point cumulants

$$\gamma_{ijk}^{(0)}(123) = -\gamma_{iu}^{(0)}(1) \gamma_{jv}^{(0)}(2) \gamma_{kw}^{(0)}(3) G_{uvw}(123). \quad (110)$$

These can be found to be given by

$$\gamma_{\rho\rho\rho}^{(0)}(123) = \gamma_{BBB}^{(0)}(123) = 0, \quad (111)$$

$$\beta \gamma_{B\rho\rho}^{(0)}(123) = -\frac{1}{\rho_0^2} \left[ \bar{K}_{12} G_2^{-1,*} + \bar{K}_{13} G_3^{-1,*} \right] \delta(1+2+3) = \frac{1}{\rho_0^2} [1 - iE_1] \delta(1+2+3), \quad (112)$$

and

$$\beta \gamma_{BB\rho}^{(0)}(123) = -2 \frac{1}{\rho_0^2} \bar{K}_{12} \delta(1+2+3) \quad (113)$$

where

$$\bar{K}_{ij} = \frac{K_{ij}}{\kappa_i \kappa_j}, \quad (114)$$

$$\delta(1+2+3) = (2\pi)^d \delta(q_1 + q_2 + q_3) 2\pi \delta(\omega_1 + \omega_2 + \omega_3) \quad (115)$$

and

$$E_1 = \omega_2 \bar{K}_{12} + \omega_3 \bar{K}_{13}. \quad (116)$$

The other vertices can be constructed using symmetry.

## VI. FIRST ORDER RESULT FOR $K$

Going to first order in the potential we have

$$\Delta W^{(1)} = \sum_u F_u G_u. \quad (117)$$

We next need to compute

$$\frac{\delta}{\delta G_j} \Delta W^{(1)} = F_j \quad (118)$$

which goes into Eq.(34) giving the result

$$c_{ij} = \langle \phi_i F_j \rangle = \sum_u \mathcal{G}_{iu} \sigma_{uj}. \quad (119)$$

Putting this result into Eq.(38) and using Eq.(36) gives the very simple result

$$K_{ij}^{(1)} = -\sigma_{ij}. \quad (120)$$

These results satisfy the FDT in a trivial way:

$$K_{\rho B}^{(1)} = K_{B\rho}^{(1)} = -\beta V(q) \quad (121)$$

and

$$K_{BB}^{(1)} = -\frac{2}{\beta\omega} \text{Im} K_{B\rho}^{(1)} = 0. \quad (122)$$

## VII. FULL FIRST ORDER SOLUTION

In FTSPD we worked out the first order theory concentrating on the two-point cumulant. Here we work things out including the equation of state and one-point averages. This sets the stage for the second order calculation.

At first order in perturbation theory<sup>23</sup>, we have the equation of state

$$G_i = G_i^{(0)} + \tilde{T}r\phi_i\Delta W^{(1)} + \dots \quad (123)$$

and for the two-point cumulant, the kinetic equation

$$G_{ij} = G_{ij}^{(0)} + \tilde{T}r\phi_i\phi_j\Delta W^{(1)} + G_{i\ell}^{(0)}\sigma_{\ell u}G_{uj}. \quad (124)$$

First, we rewrite the first order static term

$$\begin{aligned} G_i^{(1)} &= \tilde{T}r\phi_i\Delta W^{(1)} = \tilde{T}r\phi_i F_u G_u \\ &= \tilde{T}r\phi_i\phi_\ell\sigma_{\ell u}G_u = G_{i\ell}^{(0)}\sigma_{\ell u}G_u \end{aligned} \quad (125)$$

and the two-point function

$$\begin{aligned} \mathcal{G}_{ij}^{(1)} &= \tilde{T}r\phi_i\phi_j\Delta W^{(1)} = \tilde{T}r\phi_i\phi_j F_u G_u \\ &= \tilde{T}r\phi_i\phi_j\phi_\ell\sigma_{\ell u}G_u = G_{ij\ell}^{(0)}\sigma_{\ell u}G_u. \end{aligned} \quad (126)$$

Thus, one has the coupled set of equations

$$G_i = G_i^{(0)} + G_{i\ell}^{(0)}\sigma_{\ell u}G_u \quad (127)$$

and

$$G_{ij} = G_{ij}^{(0)} + G_{ij\ell}^{(0)}\sigma_{\ell u}G_u + G_{i\ell}^{(0)}\sigma_{\ell u}G_{uj} \quad (128)$$

where in the field theory protocol

$$\sigma_{ij}(k) = V(k) \left[ \hat{\rho}_i \hat{B}_j + \hat{B}_i \hat{\rho}_j \right]. \quad (129)$$

Let us look first at the term with the cubic cumulant

$$\mathcal{G}_{ij}^{(1)} = G_{ij\ell}^{(0)}\sigma_{\ell u}G_u. \quad (130)$$

We can write

$$G_{ij\ell}^{(0)} = -G_{iu}^{(0)} G_{jv}^{(0)} G_{\ell w}^{(0)} \gamma_{uvw}^{(0)} \quad (131)$$

and thus

$$\begin{aligned} \mathcal{G}_{ij}^{(1)} &= -G_{iu}^{(0)} G_{jv}^{(0)} G_{\ell w}^{(0)} \gamma_{uvw}^{(0)} \sigma_{\ell s} G_s \\ &= -G_{iu}^{(0)} G_{jv}^{(0)} \gamma_{uvw}^{(0)} (G_w - G_w^{(0)}) \end{aligned} \quad (132)$$

where in the last step we used the equation of state, Eq.(127). If we use the useful identity

$$\gamma_{uvw}^{(0)} G_w^{(0)} = -\gamma_{uv}^{(0)} \quad (133)$$

and realize that we can write

$$G_i = \frac{\bar{\rho}}{\rho_0} G_i^{(0)} \quad (134)$$

where  $\bar{\rho} = \langle \rho \rangle$ , we have

$$\begin{aligned} \mathcal{G}_{ij}^{(1)} &= -G_{iu}^{(0)} G_{jv}^{(0)} [-\gamma_{uv}^{(0)} (\bar{\rho}/\rho_0 - 1)] \\ &= G_{ij}^{(0)} (\bar{\rho}/\rho_0 - 1). \end{aligned} \quad (135)$$

The two-point equation becomes

$$\begin{aligned} G_{ij} &= G_{ij}^{(0)} + G_{ij}^{(0)} (\bar{\rho}/\rho_0 - 1) + G_{i\ell}^{(0)} \sigma_{\ell u} G_{uj} \\ &= \frac{\bar{\rho}}{\rho_0} G_{ij}^{(0)} + G_{i\ell}^{(0)} \sigma_{\ell u} G_{uj}. \end{aligned} \quad (136)$$

Now  $\bar{\rho}/\rho_0$  is determined by the equation of state. If we assume the one-point average is of the form

$$G_u(1) = \hat{\rho}_u G_\rho(q_1) 2\pi \delta(\omega_1) \quad (137)$$

then we have

$$\hat{\rho}_i [G_\rho(q_1) - G_\rho^{(0)}(q_1)] 2\pi \delta(\omega_1) = G_{i\ell}^{(0)}(q_1, \omega_1) \sigma_{\ell u}(q_1) G_u(q_1, \omega_1)$$

$$\begin{aligned}
&= G_{i\ell}^{(0)}(q_1, 0) \sigma_{\ell u}(q_1) \hat{\rho}_u G_\rho(q_1) 2\pi \delta(\omega_1) \\
&= G_{i\ell}^{(0)}(q_1, 0) \sigma_{\ell \rho}(q_1) G_\rho(q_1) 2\pi \delta(\omega_1) \\
&= G_{iB}^{(0)}(q_1, 0) V(q_1) G_\rho(q_1) 2\pi \delta(\omega_1) \\
&= \hat{\rho}_i G_{\rho B}^{(0)}(q_1, 0) V(q_1) G_\rho(q_1) 2\pi \delta(\omega_1) \\
&= \hat{\rho}_i (-\rho_0) \beta V(q_1) G_\rho(q_1) 2\pi \delta(\omega_1).
\end{aligned} \tag{138}$$

Canceling common factors gives

$$G_\rho(q) = G_\rho^{(0)}(q) - \rho_0 \beta V(q) G_\rho(q) \tag{139}$$

or

$$G_\rho(q) = \frac{1}{1 + \rho_0 \beta V(q)} G_\rho^{(0)}(q). \tag{140}$$

In the homogeneous limit

$$\bar{\rho} = \frac{\rho_0}{1 + \rho_0 \beta V(0)}. \tag{141}$$

Turn next to the two-point correlations which satisfy Eq.(136). Taking the  $\rho B$  matrix element, one gets a closed equation

$$G_{\rho B}(1) = (\bar{\rho}/\rho_0) G_{\rho B}^{(0)}(1) + G_{\rho B}^{(0)}(1) V(q_1) G_{\rho B}(1) \tag{142}$$

which can be solved to give

$$G_{\rho B}(q_1) = \frac{(\bar{\rho}/\rho_0) G_{\rho B}^{(0)}(1)}{1 - G_{\rho B}^{(0)}(1) V(q_1)} \tag{143}$$

$$= -\frac{\beta \bar{\rho} \kappa_1}{-i\omega_1 + \kappa_1 [1 + \tilde{V}(q_1)]} \tag{144}$$

where  $\kappa_1 = \bar{D} q_1^2$  and  $\tilde{V}(q_1) = \rho_0 \beta V(q_1)$ . One can then solve for the density-density correlation function

$$G_{\rho\rho}(1) = (\bar{\rho}/\rho_0) G_{\rho\rho}^{(0)}(1) + G_{\rho\rho}^{(0)}(1) V(q_1) G_{B\rho}(1) + G_{\rho B}^{(0)}(1) V(q_1) G_{\rho\rho}(1) \tag{145}$$

or

$$G_{\rho\rho}(1) = \frac{1}{1 - G_{\rho B}^{(0)}(1)V(q_1)} \left( (\bar{\rho}/\rho_0)G_{\rho\rho}^{(0)}(1) + G_{\rho\rho}^{(0)}(1)V(q_1)G_{B\rho}(1) \right). \quad (146)$$

Putting in the results for the zeroth order correlations and

$$G_{B\rho}^{(1)}(1) = -\frac{\bar{\rho}\beta\kappa_1}{i\omega_1 + \kappa_1[1 + \tilde{V}(q_1)]} \quad (147)$$

leads to the final result

$$G_{\rho\rho}(1) = \frac{2\bar{\rho}\kappa_1}{\omega_1^2 + \kappa_1^2[1 + \tilde{V}(q_1)]^2}. \quad (148)$$

Turning to the statics, we can use the result found earlier

$$-\beta S(q) = G_{\rho B}(q, 0) = \frac{-\bar{\rho}\beta\kappa}{\kappa[1 + \tilde{V}(q_1)]} \quad (149)$$

or

$$S(q) = \frac{\bar{\rho}}{1 + \tilde{V}(q_1)}. \quad (150)$$

Comparing Eq.(150) with the static Ornstein-Zernike<sup>19</sup> relation we can identify the effective interaction

$$V_{EFF}(q) = -\beta^{-1}c_D(q) \quad (151)$$

where  $c_D(q)$  is the physical direct correlation function which is assumed to be known by other means. We can, for example, assume that  $c_D(q)$  is given in the Percus-Yevick approximation for hard spheres<sup>6</sup>.

## VIII. SELF-CONSISTENT COLLECTIVE SELF-ENERGY AT SECOND ORDER

The evaluation of the collective part of the self-energy,  $K$ , at second order begins with determining  $f_j$ , defined by

$$f_j = \frac{\delta}{\delta G_j} \Delta W \quad (152)$$

at second order. We have

$$\Delta W^{(2)} = \frac{1}{2} F_u F_v G_{uv} \quad (153)$$



and

$$f_j^{(2)} = \frac{\delta \Delta W^{(2)}}{\delta G_j} = \frac{1}{2} F_u F_v \frac{\delta G_{uv}}{\delta G_j}. \quad (154)$$

We then have the standard functional manipulations,

$$\begin{aligned} \frac{\delta}{\delta G_k} G_{ij} &= - \sum_{uv} G_{iu} \frac{\delta}{\delta G_k} G_{uv}^{-1} G_{vj} \\ &= - \sum_{uv} G_{iu} G_{jv} \Gamma_{uvk}^{(3)} \end{aligned} \quad (155)$$

where we introduce the three-point vertex

$$\Gamma_{ijk} = \frac{\delta}{\delta G_k} \Gamma_{ij}. \quad (156)$$

Putting this back into Eq.(154) gives

$$f_j^{(2)} = \frac{\delta \Delta W^{(2)}}{\delta G_j} = -\frac{1}{2} F_\ell F_n G_{\ell u} G_{nv} \Gamma_{uvj} \quad (157)$$

This in turn goes into Eq.(34) and

$$\begin{aligned} c_{ij}^{(2)} &= -\frac{1}{2} \tilde{T}r \phi_i e^{\Delta W} F_\ell F_n G_{\ell u} G_{nv} \Gamma_{uvj} \\ &= -\frac{1}{2} \mathcal{G}_{ils} \sigma_{\ell n} \sigma_{sm} G_{nu} G_{mv} \Gamma_{uvj} \end{aligned}$$

where

$$\mathcal{G}_{ils} = \tilde{T}r \phi_i \phi_\ell \phi_s e^{\Delta W} \quad (158)$$

is a three-point self-correlation. Things can be written more symmetrically if we introduce the three-point self-vertex  $\gamma_{ijk}$  via

$$\mathcal{G}_{ils} = -\mathcal{G}_{iu} \mathcal{G}_{lv} \mathcal{G}_{sw} \gamma_{uvw}. \quad (159)$$

Then, the collective part of the two-point vertex is given at second order by

$$\begin{aligned} K_{ij} &= -\frac{1}{2} \gamma_{in} \mathcal{G}_{nn'} \mathcal{G}_{\ell\ell'} \mathcal{G}_{ss'} \gamma_{n'\ell's'} \sigma_{\ell u} \sigma_{sv} G_{ur} G_{vq} \Gamma_{jr q} \\ &= -\frac{1}{2} \gamma_{i\ell's'} \mathcal{G}_{\ell\ell'} \mathcal{G}_{ss'} \sigma_{\ell u} \sigma_{sv} G_{ur} G_{vq} \Gamma_{rqj} \end{aligned}$$

$$= -\frac{1}{2}\gamma_{iuv}\bar{G}_{uw}\bar{G}_{vz}\Gamma_{wzj}$$

where we have the self-dressed propagators

$$\bar{G}_{ur} = \mathcal{G}_{uv}\sigma_{vs}G_{sr}. \quad (160)$$

We see already the structure for making vertex corrections. At lowest order in the interaction we have

$$\Gamma_{ijk}^{(0)} = \gamma_{ijk}^{(0)} \quad (161)$$

and we have the nontrivial approximation for the second order contribution to the collective part of the two point vertex (self-energy) given by

$$K_{ij}^{(2)} = -\frac{1}{2}\gamma_{iuv}^{(0)}\bar{G}_{ur}\bar{G}_{vq}\gamma_{krq}^{(0)}. \quad (162)$$

Clearly  $K$  can be constructed to be symmetric and therefore  $\bar{G}$  can be constructed to be symmetric:

$$\bar{G}_{ij} = \frac{1}{2}(\mathcal{G}_{iv}\sigma_{vs}G_{sj} + G_{is}\sigma_{sv}\mathcal{G}_{vj}). \quad (163)$$

Equation (162) is the key result to be analyzed carefully. We have a collective contribution to the two-point vertex which has the following desired properties:

- (i) It is quadratic functional of the physical density-density correlation function.
- (ii) We will show that it satisfies the FDT.
- (iii) In the short-time limit, it gives the correct static contribution to the static structure factor at second order in the effective potential.
- (iv) It determines the phase diagram for ENE transitions.

In addition to the collective contribution to the two-point vertex, there is a single-particle contribution. This part of the self-energies is very interesting and will be fully treated in a companion paper.

## IX. SELF-DRESSING PROPAGATORS

### A. Second order self-energies

It appears not to be a coincidence that the matrix propagator

$$\bar{G}_{ij} = \frac{1}{2}\sum_{uv}\left[G_{iu}^{(0)}\sigma_{uv}G_{vj} + G_{iu}\sigma_{uv}G_{vj}^{(0)}\right] \quad (164)$$

appears in the one-loop expression for the collective part of the second order self-energy. In treating the single-particle contribution to the second order self-energy we find another quantity

$$\tilde{G}_{ij} = \sum_{uvpq} G_{iu}^{(0)} \sigma_{uv} G_{vp} \sigma_{pq} G_{qj}^{(0)}, \quad (165)$$

which appears in the theory. These *complications* turn out to be welcome since  $\bar{G}$  and  $\tilde{G}$  can be treated as effective matrix propagators which satisfy the FDT themselves. They also approach zero faster than  $G$  as  $q$  and  $\omega$  go to infinity, thus ensuring convergence of integrals in perturbation theory. We expect additional similar quantities to appear at higher order in perturbation theory.

### B. $\bar{G}$ -frequency regime

Consider the effective matrix propagator in Fourier space  $[(1 = (q_1, \omega_1)]$  given by

$$\bar{G}_{\alpha\beta}(1) = \frac{1}{2} \sum_{\mu\nu} \left[ G_{\alpha\mu}^{(0)}(1) \sigma_{\mu\nu}(1) G_{\nu\beta}(1) + G_{\alpha\mu}(1) \sigma_{\mu\nu}(1) G_{\nu\beta}^{(0)}(1) \right]. \quad (166)$$

We assume here that we are working in the field-theory protocol where

$$\sigma_{\mu\nu}(k) = V(k)(\hat{\rho}_\mu \hat{B}_\nu + \hat{\rho}_\nu \hat{B}_\mu). \quad (167)$$

Taking components of Eq.(166) we see that the symmetrization does not influence the response contributions:

$$\begin{aligned} \bar{G}_{\rho B}(1) &= \frac{1}{2} \sum_{\mu\nu} \left[ G_{\rho\mu}^{(0)}(1) \sigma_{\mu\nu}(1) G_{\nu B}(1) + G_{\rho\mu}(1) \sigma_{\mu\nu}(1) G_{\nu B}^{(0)}(1) \right] \\ &= \frac{1}{2} \sum_{\mu} \left[ G_{\rho\mu}^{(0)}(1) \sigma_{\mu\rho}(1) G_{\rho B}(1) + G_{\rho\mu}(1) \sigma_{\mu\rho}(1) G_{\rho B}^{(0)}(1) \right] \\ &= \frac{1}{2} \left[ G_{\rho B}^{(0)}(1) V(1) G_{\rho B}(1) + G_{\rho B}(1) V(1) G_{\rho B}^{(0)}(1) \right] \\ &= G_{\rho B}^{(0)}(1) V(1) G_{\rho B}(1). \end{aligned} \quad (168)$$

$\bar{G}_{\rho B}$  and  $G_{\rho B}$  have the same analytic structure; they are analytic in the upper half-plane. Next,

$$\bar{G}_{BB} = 0, \quad (169)$$

while for the density-density component,

$$\begin{aligned}
\bar{G}_{\rho\rho}(1) &= \frac{1}{2} \sum_{\mu\nu} \left[ G_{\rho\mu}^{(0)}(1) \sigma_{\mu\nu}(1) G_{\nu\rho}(1) + G_{\rho\mu}(1) \sigma_{\mu\nu}(1) G_{\nu\rho}^{(0)}(1) \right] \\
&= \frac{1}{2} V(1) \left[ G_{\rho B}^{(0)}(1) G_{\rho\rho}(1) + G_{\rho\rho}^{(0)}(1) G_{B\rho}(1) + G_{\rho B}(1) G_{\rho\rho}^{(0)}(1) + G_{\rho\rho}(1) G_{B\rho}^{(0)}(1) \right] \\
&= \frac{1}{2} V(1) \left[ G_{\rho\rho}^{(0)}(1) (G_{B\rho}(1) + G_{\rho B}(1)) + G_{\rho\rho}(1) (G_{B\rho}^{(0)}(1) + G_{\rho B}^{(0)}(1)) \right] \\
&= G_{\rho\rho}^{(0)}(1) V(1) \text{Re} G_{\rho B}(1) + G_{\rho\rho}(1) V(1) \text{Re} G_{\rho B}^{(0)}(1)
\end{aligned} \tag{170}$$

which is real but not necessarily positive. It is crucial to realize that  $\bar{G}$  itself satisfies the FDT if  $G$  and  $G^{(0)}$  satisfy the FDT.

The proof is as follows. Starting with

$$\bar{G}_{\rho B}(1) = G_{\rho B}^{(0)}(1) V(1) G_{\rho B}(1) \tag{171}$$

and assuming  $V(1)$  is real, we take the imaginary part,

$$\text{Im } \bar{G}_{\rho B}(1) = \text{Im } G_{\rho B}^{(0)}(1) V(1) \text{Re } G_{\rho B}(1) + \text{Re } G_{\rho B}^{(0)}(1) V(1) \text{Im } G_{\rho B}(1). \tag{172}$$

Multiplying by  $-2/(\beta\omega_1)$ , we have

$$\begin{aligned}
-\frac{2}{\beta\omega_1} \text{Im } \bar{G}_{\rho B}(1) &= -\frac{2}{\beta\omega_1} \left( \text{Im } G_{\rho B}^{(0)}(1) V(1) \text{Re } G_{\rho B}(1) + \text{Re } G_{\rho B}^{(0)}(1) V(1) \text{Im } G_{\rho B}(1) \right) \\
&= G_{\rho\rho}^{(0)}(1) V(1) \text{Re } G_{\rho B}(1) + \text{Re } G_{\rho B}^{(0)}(1) V(1) G_{\rho\rho}(1) \\
&= \bar{G}_{\rho\rho}(1).
\end{aligned} \tag{173}$$

Thus  $\bar{G}$  satisfies the FDT

$$\bar{G}_{\rho\rho}(\omega) = -\frac{2}{\beta\omega} \text{Im } \bar{G}_{\rho B}(\omega) \tag{174}$$

and we can write

$$\bar{G}_{\rho B}(\omega) = \int \frac{d\bar{\omega}}{2\pi} \frac{\beta\bar{\omega} \bar{G}_{\rho\rho}(\bar{\omega})}{\omega - \bar{\omega} + i\eta} \tag{175}$$

and

$$\bar{G}_{B\rho}(\omega) = \int \frac{d\bar{\omega}}{2\pi} \frac{\beta\bar{\omega} \bar{G}_{\rho\rho}(\bar{\omega})}{\omega - \bar{\omega} - i\eta}. \tag{176}$$

### C. $\bar{G}$ -time domain

In the time domain we have the convolution

$$\begin{aligned}\bar{G}_{\rho\rho}(t) &= \frac{1}{2}V(k) \int_{-\infty}^{\infty} ds (G_{B\rho}(t-s) + G_{\rho B}(t-s)) G_{\rho\rho}^{(0)}(s) \\ &+ \frac{1}{2}V(k) \int_{-\infty}^{\infty} ds G_{\rho\rho}(t-s) (G_{B\rho}^{(0)}(s) + G_{\rho B}^{(0)}(s)).\end{aligned}$$

This together with the fluctuation-dissipation theorem leads to the short-time results

$$\bar{G}_{\rho\rho}(0) = -\beta V(k) \rho_0 S(k)$$

$$\dot{\bar{G}}_{\rho\rho}(0) = 0$$

$$\ddot{\bar{G}}_{\rho\rho}(0) = \beta V(k) \dot{\bar{G}}_{\rho\rho}(0) \dot{\bar{G}}_{\rho\rho}^{(0)}(0) = 0. \quad (177)$$

### X. SECOND ORDER COLLECTIVE SELF-ENERGY AND THE FDT

We have the crucial one-loop contribution to the self-energy

$$\Gamma_{\alpha\beta}^{(2,C)}(12) = -\frac{1}{2} \int d3d4d5d6 \gamma_{\alpha\mu\nu}^{(0)}(134) \bar{G}_{\mu\sigma}(35) \bar{G}_{\nu q}(46) \gamma_{\beta\sigma q}^{(0)}(256).$$

In terms of Fourier transforms in space and time we find

$$\Gamma_{\alpha\beta}^{(2,C)}(p_1, p_2) = (2\pi)^{d+1} \delta(p_1 + p_2) \Gamma_{\alpha\beta}^{(2,C)}(p_1) \quad (178)$$

and

$$\begin{aligned}\Gamma_{\alpha\beta}^{(2,C)}(-p_1) &= - \int dp_3 dp_4 \frac{1}{2} \gamma_{\alpha\mu\nu}^{(0)*}(134) \delta(p_1 + p_3 + p_4) \\ &\times \bar{G}_{\mu\sigma}(3) \bar{G}_{\nu q}(4) \gamma_{\beta\sigma q}^{(0)}(1, 3, 4)\end{aligned} \quad (179)$$

where we have introduced the notation

$$\int dp_3 = \int \frac{d\omega_3}{2\pi} \int \frac{d^d k_3}{(2\pi)^d}. \quad (180)$$

$\bar{G}$  is a correlation function that satisfies the fluctuation-dissipation theorem in the form

$$\bar{G}_{\rho B}(\omega) = \int \frac{d\bar{\omega}}{2\pi} \frac{\beta \bar{\omega} \bar{G}_{\rho\rho}(\bar{\omega})}{\omega - \bar{\omega} + i\eta} \quad (181)$$

and

$$\bar{G}_{B\rho}(\omega) = \int \frac{d\bar{\omega}}{2\pi} \frac{\beta \bar{\omega} \bar{G}_{\rho\rho}(\bar{\omega})}{\omega - \bar{\omega} - i\eta}. \quad (182)$$

### A. $\Gamma_{B\rho}$

We can break Eq.(179) up into components and associate a set of one-loop contributions which differ by different vertices and propagators. A number of self-energy contributions vanish due to causality and for  $\Gamma_{B\rho}$  we obtain three contributions. (To simplify the notation we suppress the superscript 0 on the three-point vertices.) Thus

$$\Gamma_{B\rho}^{(2,C,1)}(-p_1) = -\frac{1}{2} \int dp_3 dp_4 \gamma_{B\rho\rho}^*(134) \delta(p_1 + p_3 + p_4) \bar{G}_{\rho B}(3) \bar{G}_{\rho B}(4) \gamma_{\rho BB}(134), \quad (183)$$

$$\Gamma_{B\rho}^{(2,C,2)}(-p_1) = -\frac{1}{2} \int dp_3 dp_4 \gamma_{B\rho\rho}^*(134) \delta(p_1 + p_3 + p_4) \bar{G}_{\rho B}(3) \bar{G}_{\rho\rho}(4) \gamma_{\rho B\rho}(134), \quad (184)$$

and

$$\Gamma_{B\rho}^{(2,C,3)}(-p_1) = -\frac{1}{2} \int dp_3 dp_4 \gamma_{B\rho\rho}^*(134) \delta(p_1 + p_3 + p_4) \bar{G}_{\rho B}(4) \bar{G}_{\rho\rho}(3) \gamma_{\rho B\rho}(134). \quad (185)$$

We want to write these expressions in terms of  $G_{\rho\rho}$  and we must exhibit care in treating the frequency integrals. Noting that  $\beta^2 \gamma_{\rho BB}(134) = -2\bar{K}_{34}$ , we have

$$\begin{aligned} \beta \Gamma_{B\rho}^{(2,C,1)}(-p_1) &= -\frac{1}{2} \int dp_3 dp_4 \beta \gamma_{B\rho\rho}^*(134) \delta(p_1 + p_3 + p_4) \beta^{-1} \bar{G}_{\rho B}(3) \beta^{-1} \bar{G}_{\rho B}(4) (-2\bar{K}_{34}) \\ &= \int dp_3 dp_4 \beta \gamma_{B\rho\rho}^*(134) \delta(p_1 + p_3 + p_4) \beta^{-1} \bar{G}_{\rho B}(3) (\bar{K}_{34}) \int \frac{d\bar{\omega}_4}{2\pi} \frac{\bar{\omega}_4 \bar{G}_{\rho\rho}(\bar{\omega}_4)}{\omega_4 - \bar{\omega}_4 + i\eta} \\ &= \int dp_3 dp_4 \bar{K}_{34} \int \frac{d\bar{\omega}_4}{2\pi} \bar{\omega}_4 \bar{G}_{\rho\rho}(\bar{\omega}_4) \beta \gamma_{B\rho\rho}^*(134) \delta(q_1 + k_3 + k_4) \delta(\omega_1 + \omega_3 + \omega_4) \\ &\quad \times \beta^{-1} \bar{G}_{\rho B}(3) \frac{1}{\omega_4 - \bar{\omega}_4 + i\eta} \\ &= \int dk_3 dk_4 \bar{K}_{34} \delta(q_1 + k_3 + k_4) \int \frac{d\bar{\omega}_4}{2\pi} \bar{\omega}_4 \bar{G}_{\rho\rho}(\bar{\omega}_4) \\ &\quad \times \int \frac{d\omega_3}{2\pi} \beta \gamma_{B\rho\rho}^*(134) \beta^{-1} \bar{G}_{\rho B}(3) \frac{1}{-\omega_1 - \omega_3 - \bar{\omega}_4 + i\eta} \\ &= (-1) \int dk_3 dk_4 \bar{K}_{34} \delta(q_1 + k_3 + k_4) \int \frac{d\bar{\omega}_4}{2\pi} \bar{\omega}_4 \bar{G}_{\rho\rho}(\bar{\omega}_4) \end{aligned}$$

$$\times \int \frac{d\omega_3}{2\pi} \beta \gamma_{B\rho\rho}^*(134) \beta^{-1} \bar{G}_{\rho B}(3) \frac{1}{\omega_1 + \omega_3 + \bar{\omega}_4 - i\eta}. \quad (186)$$

Now  $\bar{G}_{\rho B}(3)$  is analytic in the upper half plane. Closing the contour in the upper half plane,

$$\begin{aligned} \beta \Gamma_{B\rho}^{(2,C,1)}(-p_1) &= (-1) \int dk_3 dk_4 \bar{K}_{34} \delta(q_1 + k_3 + k_4) \int \frac{d\bar{\omega}_4}{2\pi} \beta \bar{\omega}_4 \bar{G}_{\rho\rho}(\bar{\omega}_4) \frac{(2\pi i)}{2\pi} \\ &\quad \times \beta^{-1} \bar{G}_{\rho B}(-\omega_1 - \bar{\omega}_4) \beta \gamma_{B\rho\rho}^*(1, -1 - \bar{4}, \bar{4}) \\ &= \int dk_3 dk_4 \bar{K}_{34} \delta(q_1 + k_3 + k_4) (-i \bar{K}_{34}) \int \frac{d\bar{\omega}_4}{2\pi} \int \frac{d\bar{\omega}_3}{2\pi} \bar{\omega}_4 \bar{G}_{\rho\rho}(\bar{\omega}_4) \\ &\quad \times \frac{\beta \bar{\omega}_3 \bar{G}_{\rho\rho}(\bar{\omega}_3)}{-\omega_1 - \bar{\omega}_3 - \bar{\omega}_4 + i\eta} \beta \gamma_{B\rho\rho}^*(1, -1 - \bar{4}, \bar{4}) \\ &= \int dk_3 dk_4 \bar{K}_{34} \delta(q_1 + k_3 + k_4) \int \frac{d\bar{\omega}_4}{2\pi} \int \frac{d\bar{\omega}_3}{2\pi} \beta \bar{G}_{\rho\rho}(\bar{\omega}_4) \bar{\omega}_4 \bar{\omega}_3 \\ &\quad \times \bar{G}_{\rho\rho}(\bar{\omega}_3) (i \bar{K}_{34}) R_- \beta \gamma_{B\rho\rho}^*(1, -1 - \bar{4}, \bar{4}) \\ &= \hat{\mathcal{O}}[J_{B\rho}^{(1)}], \end{aligned} \quad (187)$$

where we introduce the notation

$$\hat{\mathcal{O}}[J] = \int dk_3 dk_4 \delta(q_1 + k_3 + k_4) \int \frac{d\bar{\omega}_4}{2\pi} \int \frac{d\bar{\omega}_3}{2\pi} \bar{G}_{\rho\rho}(\bar{\omega}_3) \bar{G}_{\rho\rho}(\bar{\omega}_4) J \quad (188)$$

and

$$J_{B\rho}^{(1)} = \bar{\omega}_4 \bar{\omega}_3 (i \bar{K}_{34}) R_- \beta \gamma_{B\rho\rho}^*(1, -1 - \bar{4}, \bar{4}). \quad (189)$$

Next we notice that  $\Gamma_{B\rho}^{(2,C,2)}(-p_1) = \Gamma_{B\rho}^{(2,C,3)}(-p_1)$ , so

$$\beta \Gamma_{B\rho}^{(2+3)}(-p_1) = -2 \frac{1}{2} \int dp_3 dp_4 \beta \gamma_{B\rho\rho}^*(134) \delta(p_1 + p_3 + p_4)$$

$$\times \beta^{-1} \bar{G}_{\rho B}(4) \bar{G}_{\rho\rho}(3) \beta \gamma_{\rho\rho B}(134)$$

$$= - \int dk_3 dk_4 \delta(q_1 + k_3 + k_4) \int d\bar{\omega}_3 \beta \gamma_{B\rho\rho}^*(1\bar{3}, -1 - \bar{3}) \bar{G}_{\rho\rho}(3)$$

$$\begin{aligned}
& \times \int d\bar{\omega}_4 \frac{\bar{\omega}_4 \bar{G}_{\rho\rho}(\bar{4})}{-\omega_1 - \bar{\omega}_3 - \bar{\omega}_4 + i\eta} \beta \gamma_{\rho\rho B}(1\bar{3}, -1 - \bar{3}) \\
& = \hat{\mathcal{O}}[J_{B\rho}^{(2+3)}],
\end{aligned}$$

where

$$J_{B\rho}^{(2+3)} = \bar{\omega}_4 R_- \beta \gamma_{B\rho\rho}^*(1\bar{3}, -1 - \bar{3}) \beta \gamma_{\rho\rho B}(1\bar{3}, -1 - \bar{3}). \quad (190)$$

The total is thus given by

$$J_{B\rho} = R_- [i\bar{\omega}_4 \bar{\omega}_3 \bar{K}_{34} \beta \gamma_{B\rho\rho}^*(1, -1 - \bar{4}, \bar{4}) + \bar{\omega}_4 \beta \gamma_{B\rho\rho}^*(1\bar{3}, -1 - \bar{3}) \beta \gamma_{\rho\rho B}(1\bar{3}, -1 - \bar{3})].$$

We next need the vertices

$$\beta \gamma_{B\rho\rho}^*(1, -1 - \bar{4}, \bar{4}) = 1 + iE_1 - i\Omega \bar{K}_{13}, \quad (191)$$

$$\beta \gamma_{B\rho\rho}^*(1\bar{3}, -1 - \bar{3}) = 1 + iE_1 - i\Omega \bar{K}_{14}, \quad (192)$$

and

$$\beta \gamma_{\rho\rho B}(1\bar{3}, -1 - \bar{3}) = 1 - iE_4, \quad (193)$$

where

$$\Omega = \omega_1 + \bar{\omega}_3 + \bar{\omega}_4 \quad (194)$$

and

$$E_4 = \omega_1 \bar{K}_{14} + \bar{\omega}_3 \bar{K}_{34}. \quad (195)$$

We then have

$$J_{B\rho} = R_- [i\bar{\omega}_4 \bar{\omega}_3 \bar{K}_{34} [1 + iE_1 - i\Omega \bar{K}_{13}] + \bar{\omega}_4 (1 + iE_1 - i\Omega \bar{K}_{14}) (1 - iE_4)]. \quad (196)$$

If we group together the terms proportional to  $\Omega$ , set  $R_- \Omega = 1$ , and notice that inside the integrations each term vanishes because of odd frequency integrals over  $\bar{G}_{\rho\rho}$ , we then have

$$J_{B\rho} = R_- [i\bar{\omega}_4 \bar{\omega}_3 \bar{K}_{34} [1 + iE_1] + \bar{\omega}_4 (1 + iE_1) (1 - iE_4)]$$



$$\begin{aligned}
&= R_-[1 + iE_1][i\bar{\omega}_4\bar{\omega}_3\bar{K}_{34} + \bar{\omega}_4(1 - iE_4)] \\
&= R_-[1 + iE_1][i\bar{\omega}_4\bar{\omega}_3\bar{K}_{34} + \bar{\omega}_4(1 - i(\omega_1\bar{K}_{14} + \bar{\omega}_3\bar{K}_{34}))] \\
&= R_-[1 + iE_1][\bar{\omega}_4(1 - i\omega_1\bar{K}_{14})].
\end{aligned} \tag{197}$$

Inside the integrals we are free to symmetrize with respect to  $3 \leftrightarrow 4$ :

$$\begin{aligned}
J_{B\rho} &= R_-[1 + iE_1]\left[\frac{1}{2}[\bar{\omega}_4 + \bar{\omega}_3] - i\frac{\omega_1}{2}E_1\right] \\
&= \frac{1}{2}R_-[1 + iE_1][\Omega - \omega_1 - i\omega_1E_1]R_- \\
&= \frac{1}{2}[1 + iE_1] - \frac{\omega_1}{2}[1 + iE_1]^2R_-
\end{aligned}$$

and

$$\beta\Gamma_{B\rho}(-p_1) = \hat{\mathcal{O}}\left[\frac{1}{2}[1 + iE_1] - \frac{\omega_1}{2}[1 + iE_1]^2R_-\right]. \tag{198}$$

Since  $\hat{\mathcal{O}}[\frac{1}{2}iE_1] = 0$  we have

$$\beta\Gamma_{B\rho}^{(2,C)}(-p_1) = \hat{\mathcal{O}}\left[\frac{1}{2} - \frac{\omega_1}{2}[1 + iE_1]^2R_-\right] \tag{199}$$

or

$$\beta\Gamma_{B\rho}^{(2,C)}(p_1) = \tilde{\mathcal{O}}\left[\frac{1}{2} + \frac{\omega_1}{2}\tilde{R}_-[1 + iE_1]^2\right], \tag{200}$$

where

$$\tilde{R}_- = \frac{1}{\bar{\omega}_3 + \bar{\omega}_4 - \omega_1 - i\eta} \tag{201}$$

and

$$\tilde{\mathcal{O}}[J] = \int dk_3 dk_4 \delta(-q_1 + k_3 + k_4) \int \frac{d\bar{\omega}_4}{2\pi} \int \frac{d\bar{\omega}_3}{2\pi} \bar{G}_{\rho\rho}(\bar{\omega}_3) \bar{G}_{\rho\rho}(\bar{\omega}_4) J. \tag{202}$$

We need the result

$$Im \beta\Gamma_{B\rho}^{(2,C)}(p_1) = \frac{\omega_1}{2}\hat{\mathcal{O}}[\tilde{R}_-[1 + iE_1]^2]. \tag{203}$$

### B. $\Gamma_{BB}$

We turn next to the second order self-energy with two  $B$ 's. After using causality, there are five nonzero graphs. The first is the simplest and given by

$$\beta^2 \Gamma_{BB}^{(2,C,0)}(-p_1) = -\frac{1}{2} \int dp_3 dp_4 \beta \gamma_{B\rho\rho}^*(134) \delta(p_1 + p_3 + p_4) \bar{G}_{\rho\rho}(3) \bar{G}_{\rho\rho}(4) \beta \gamma_{B\rho\rho}(134),$$

while there are four similar contributions given by

$$\beta^2 \Gamma_{BB}^{(2,C,1)}(-p_1) = -\frac{1}{2} \int dp_3 dp_4 \beta \gamma_{B\rho\rho}^*(134) \delta(p_1 + p_3 + p_4) \beta^{-1} \bar{G}_{\rho B}(3) \bar{G}_{\rho\rho}(4) \beta^2 \gamma_{BB\rho}(134),$$

$$\beta^2 \Gamma_{BB}^{(2,C,2)}(-p_1) = -\frac{1}{2} \int dp_3 dp_4 \beta \gamma_{B\rho\rho}^*(134) \delta(p_1 + p_3 + p_4) \bar{G}_{\rho\rho}(3) \beta^{-1} \bar{G}_{\rho B}(4) \beta^2 \gamma_{B\rho B}(134),$$

$$\beta^2 \Gamma_{BB}^{(2,C,3)}(-p_1) = -\frac{1}{2} \int dp_3 dp_4 \beta^2 \gamma_{B\rho B}^*(134) \delta(p_1 + p_3 + p_4) \bar{G}_{\rho\rho}(3) \beta^{-1} \bar{G}_{B\rho}(4) \beta \gamma_{B\rho\rho}(134),$$

and

$$\beta^2 \Gamma_{BB}^{(2,C,4)}(-p_1) = -\frac{1}{2} \int dp_3 dp_4 \beta^2 \gamma_{BB\rho}^*(134) \delta(p_1 + p_3 + p_4) \beta^{-1} \bar{G}_{B\rho}(3) \bar{G}_{\rho\rho}(4) \beta \gamma_{B\rho\rho}(134).$$

Then, the simplest graph can be rewritten as

$$\beta^2 \Gamma_{BB}^{(2,C,0)}(-p_1) = \hat{\mathcal{O}}[J_{BB}^{(0)}] \quad (204)$$

where

$$J_{BB}^{(0)} = -\frac{1}{2} \delta(\Omega) |\gamma_{B\rho\rho}(134)|^2 \quad (205)$$

$$= i \frac{1}{2} (R_- - R_+) [1 + E_1^2]. \quad (206)$$

Turning to the other four contributions, they can be grouped together in a way that shows their sum is real

$$\begin{aligned} \beta^2 \Gamma_{BB}^{(2,C,1-4)}(-p_1) &= \int dp_3 dp_4 \delta(p_1 + p_3 + p_4) \bar{G}_{\rho\rho}(3) \bar{K}_{14} \\ &\times [\gamma_{B\rho\rho}^*(134) \bar{G}_{\rho B}(4) + \gamma_{B\rho\rho}(134) \bar{G}_{B\rho}(4)]. \end{aligned}$$

This leads to

$$\beta^2 \Gamma_{BB}^{(2,C,1-4)}(-p_1) = \hat{\mathcal{O}}[J_{BB}^{(1-4)}]$$

where

$$\begin{aligned}
J_{BB}^{(1-4)} &= 2\bar{\omega}_4 \bar{K}_{14} \int d\omega_4 \delta(\omega_1 + \bar{\omega}_3 + \omega_4) \left[ \frac{[1 + iE_1]}{\omega_4 - \bar{\omega}_4 + i\eta} + \frac{[1 - iE_1]}{\omega_4 - \bar{\omega}_4 - i\eta} \right] \\
&= 2\bar{\omega}_4 \bar{K}_{14} \left[ \frac{[1 + i\tilde{E}_1]}{-\omega_1 - \bar{\omega}_3 - \bar{\omega}_4 + i\eta} + \frac{[1 - i\tilde{E}_1]}{-\omega_1 - \bar{\omega}_3 - \bar{\omega}_4 - i\eta} \right] \\
&= -2\bar{\omega}_4 \bar{K}_{14} \left\{ R_- [1 + i\tilde{E}_1] + R_+ [1 - i\tilde{E}_1] \right\}
\end{aligned}$$

and

$$\tilde{E}_1 = E_1 - \Omega \bar{K}_{14}. \quad (207)$$

The terms generated from  $\tilde{E}_1$  proportional to  $\Omega$  give zero contribution after integration over  $\bar{\omega}_3$  and  $\bar{\omega}_4$ , so

$$\begin{aligned}
J_{BB}^{(1-4)} &= -2\bar{\omega}_4 \bar{K}_{14} \left\{ [R_- [1 + iE_1] + R_+ [1 - iE_1]] \right\} \\
&= -E_1 \left\{ R_- [1 + iE_1] + R_+ [1 - iE_1] \right\}.
\end{aligned}$$

Combining the two contributions gives

$$\begin{aligned}
J_{BB} &= i\frac{1}{2}(R_- - R_+)[1 + E_1^2] = -E_1 \left\{ R_- [1 + iE_1] + R_+ [1 - iE_1] \right\} \\
&= \frac{i}{2}[1 + iE_1]^2 R_- - \frac{i}{2}[1 - iE_1]^2 R_+ \\
&= -Im R_- [1 + iE_1]^2.
\end{aligned}$$

Finally we have the result

$$\beta^2 \Gamma_{BB}^{(2,C)}(p_1) = -Im \tilde{\mathcal{O}}[\tilde{R}_- [1 + iE_1]^2] \quad (208)$$

and we see that this set of self-energies satisfies the FDT as

$$Im \Gamma_{B\rho}^{(2,C)}(p_1) = -\frac{\beta\omega_1}{2} \Gamma_{BB}^{(2,C)}(p_1). \quad (209)$$

## XI. STATICS AND AN EFFECTIVE POTENTIAL APPROACH

Let us summarize our basic results up to now. The two-point vertex is given in the form

$$\Gamma_{ij} = \gamma_{ij}^{(0)} + \gamma_{ij}^{(1)} + \Gamma_{ij}^{(1,c)} + \gamma_{ij}^{(2,s)} + \Gamma_{ij}^{(2,c)} \quad (210)$$

where  $\gamma_{ij}^{(0)}$  is the noninteracting gas result,  $\gamma_{ij}^{(1)}$  and  $\Gamma_{ij}^{(1,C)}$  are the first order single-particle and collective contributions (respectively) to the self-energy, and  $\gamma_{ij}^{(2,s)}$  and  $\Gamma_{ij}^{(2,C)}$  are the single-particle and collective contributions at second order in perturbation theory. Most of the focus in this paper is on the collective part of the two-point vertex at second order. We will be able to show that the collective part determines the static structure to this order and determines the ENE phase diagram. The single-particle contribution does not enter into either determination. However, we anticipate that it plays a crucial role in the slow kinetics near the ENE transition. It will be treated in detail in a companion paper.

Let us now determine the static structure in the second order approximation. This is very conveniently done in the case where there is a linear fluctuation-dissipation theorem. The key result is that the zero frequency limit of the response function gives the static structure factor

$$G_{\rho B}(q, 0) = - \int \frac{d\omega}{2\pi} \beta G_{\rho\rho}(q, \omega) = -\beta S(q) \quad (211)$$

in the ergodic phase. Then, using the Dyson's equation we have

$$G_{\rho B}(q, 0) = \frac{1}{-1/(\beta\rho_0) - V(q) + \Gamma_{B\rho}(q, 0)} \quad (212)$$

or

$$S(q) = \frac{\rho_0}{1 + \rho_0\beta V(q) - \beta\rho_0\Gamma_{B\rho}(q, 0)}. \quad (213)$$

The needed self-energy is given by Eq.(200) as

$$\begin{aligned} \beta\Gamma_{B\rho}(q, 0) &= \beta\tilde{\mathcal{O}}\left[\frac{1}{2}\right] \\ &= \frac{1}{2\rho_0^4} \int d^3k_3 d^d k_4 (2\pi)^d \delta(-q_1 + k_3 + k_4) \bar{G}_{\rho\rho}(3) \bar{G}_{\rho\rho}(4) \\ &= \frac{1}{2\rho_0^4} \int \frac{d^d k_3}{(2\pi)^d} \frac{d^d k_4}{(2\pi)^d} (2\pi)^d \delta(q_1 + k_3 + k_4) \int \frac{d\omega_3}{2\pi} \bar{G}_{\rho\rho}(3) \int \frac{d\omega_4}{2\pi} \bar{G}_{\rho\rho}(4). \end{aligned} \quad (214)$$

We showed previously that

$$\int \frac{d\omega_3}{2\pi} \bar{G}_{\rho\rho}(3) = \bar{G}_{\rho\rho}(k_3, t=0) = -\rho_0 \beta V(k_3) S(k_3), \quad (215)$$

therefore,

$$\beta \Gamma_{B\rho}(q, 0) = \frac{1}{2\rho_0^4} \int \frac{d^d k_3}{(2\pi)^d} \frac{d^d k_4}{(2\pi)^d} (2\pi)^d \delta(q_1 + k_3 + k_4) \rho_0 \beta V(k_3) S(k_3) \rho_0 \beta V(k_4) S(k_4).$$

Then, after introducing dimensionless wavenumber  $k'_3 = k_3 \sigma$  (where  $\sigma$  is the hard-sphere diameter),  $\tilde{S}(q') = S(q)/\rho_0$ ,  $\tilde{V}(q') = \rho_0 \beta V(q)$ , and

$$\tilde{S}(q') = \frac{1}{1 + \tilde{V}(q') - M(q')}, \quad (216)$$

where

$$M(q') = \rho_0 \beta \Gamma_{B\rho}(q, 0) = \frac{\pi}{12\eta} \int \frac{d^d k'_3}{(2\pi)^d} \frac{d^d k'_4}{(2\pi)^d} \delta(q'_1 + k'_3 + k'_4) \tilde{V}(k'_3) \tilde{S}(k'_3) \tilde{V}(k'_4) \tilde{S}(k'_4), \quad (217)$$

where  $\eta = \pi \rho \sigma^3 / 6$  is the packing fraction for hard spheres. For simplicity we drop the primes on the dimensionless wavenumbers.

So far the analysis has been rather general. Let us apply these results to the case of three-dimensional hard spheres. We immediately have a problem if we view our perturbation theory expansion in the conventional way since the Fourier transform of a hard-core potential is not well defined. We can however take a different approach. Instead of taking  $V(q)$  as given and computing  $S(q)$ , we take  $S(q)$  as given and, at a given order, determine the effective potential by inverting the equivalent of Eq.(216). Thus, at first order

$$\tilde{S}(q) = \frac{1}{1 + \tilde{V}(q)} \quad (218)$$

and the effective potential is essentially the direct correlation function given by

$$\tilde{V}(q) = \frac{1}{\tilde{S}(q)} - 1. \quad (219)$$

We assume that the structure factor for a hard-sphere system is given by the solution<sup>6</sup> to the Percus-Yevick equation. In Fig. 1 we plot the structure factor for different packing fractions.

The numerical solution of Eq.(216) for  $\tilde{V}(q)$  is obtained as follows. First, rewrite Eq.(216) in the form

$$\tilde{V} = \tilde{S}^{-1} - 1 + M(\tilde{V}). \quad (220)$$

Next, define

$$V_0 = \tilde{S}^{-1} - 1 \quad (221)$$

and rewrite

$$\tilde{V} = V_0 + Q(\tilde{V}), \quad (222)$$

where

$$Q(\tilde{V}) = M[V_0 + Q(\tilde{V})] \equiv I(Q). \quad (223)$$

We seek an iterated solution. To this end, we write

$$\alpha Q_{\ell+1} + (1 - \alpha)Q_\ell = I(Q_\ell) \quad (224)$$

with the number  $\alpha$  chosen appropriately. This equation can be rewritten as a functional recursion relation,

$$Q_{\ell+1} = Q_\ell + \frac{1}{\alpha}[I(Q_\ell) - Q_\ell]. \quad (225)$$

At a fixed point we have a solution to the original problem. By trial and error we find that a reasonable choice for  $\alpha$  is  $\alpha = 100$ . Then beginning with  $Q_0 = 0$  we monitor

$$\Delta_\ell = 4 \frac{\sum_q (\tilde{V}_{\ell+1} - \tilde{V}_\ell)^2}{\sum_q (\tilde{V}_{\ell+1} + \tilde{V}_\ell)^2}. \quad (226)$$

Over the entire range of  $\eta$  studied, we find that  $\Delta_\ell$  is driven to small values ( $10^{-6}$ - $10^{-8}$ ) with a minimum controlled by the range of wavenumber included in the calculation. One obtains good accuracy if one chooses  $q_{max} = 80$ .

In Fig.2 we give the results for the effective potential for a sequence of densities. Also shown is  $V_0$ . A key quantity is  $\tilde{V}\tilde{S}$ . It is plotted in Fig. 3 where we also plot  $V_0\tilde{S}$ . Clearly the two quantities are close and do not change dramatically in going from first to second order. The biggest shift is for small wavenumbers. That  $M(q)$  has a maximum for small  $q$  is understood by assuming that  $\tilde{V}(k)\tilde{S}(k)$  is sharply peaked for  $k = k_0$ . Therefore  $\tilde{V}(k)\tilde{S}(k)\tilde{V}(k+q)\tilde{S}(k+q)$  is small except when  $k \approx |q + k| \approx k_0$  which is true for small  $q$ .

## XII. ENE TRANSITION

As we increase the density, (or lower the temperature), our model system slows down. It is possible that there is a density above which the density-density correlation does not decay to zero for long times. In the nonergodic phase

$$\lim_{t \rightarrow \infty} G_{\rho\rho}(q, t) = F(q) > 0.$$

In terms of the time Fourier transform,

$$G_{\rho\rho}(q, \omega) = F(q)2\pi\delta(\omega) + g_{\rho\rho}(q, \omega), \quad (227)$$

where  $g_{\rho\rho}$  is the *regular* contribution. In the nonergodic phase, assuming the FDT still holds, one has for the response function

$$\begin{aligned} G_{\rho B}(q, \omega = 0) &= \int_{-\infty}^{\infty} G_{\rho B}(q, t) \\ &= \beta \int_{-\infty}^{\infty} \theta(t) \frac{\partial}{\partial t} G_{\rho\rho}(q, t) \\ &= \beta \int_0^{\infty} \frac{\partial}{\partial t} G_{\rho\rho}(q, t) = \beta[F(q) - S(q)] \end{aligned} \quad (228)$$

while

$$\begin{aligned} G_{B\rho}(q, \omega = 0) &= \int_{-\infty}^{\infty} G_{B\rho}(q, t) \\ &= \beta \int_{-\infty}^{\infty} \theta(-t)(-1) \frac{\partial}{\partial t} G_{\rho\rho}(q, t) \\ &= \beta \int_{-\infty}^0 (-1) \frac{\partial}{\partial t} G_{\rho\rho}(q, t) = -\beta S(q). \end{aligned} \quad (229)$$

There are several equivalent ways of determining the nonergodicity parameter  $F$  as a function of density and temperature. One approach developed in the time-domain results from pursuing the memory-function equation, Eq.(83). This will be explored elsewhere. Here we give a more direct complementary analysis in frequency space.

Using one of the Dyson equations we have

$$G_{\rho\rho}(q, \omega) = -G_{\rho B}(q, \omega)\Gamma_{BB}(q, \omega)G_{B\rho}(q, \omega). \quad (230)$$

For an ENE transition we associate a zero-frequency delta-function in  $\Gamma_{BB}$

$$\Gamma_{BB}(q, \omega) = -2\pi\delta(\omega)\bar{\Gamma}(q) + \text{regular part.} \quad (231)$$

Then, using Eqs.(227) and (231) in Eq. (230), we find

$$F(q) = \beta^2\bar{\Gamma}(q)[S(q) - F(q)]S(q). \quad (232)$$

Equation (232) can be rewritten as

$$\frac{F(q)}{S(q) - F(q)} = S(q)\beta^2\bar{\Gamma}(q).$$

We need to extract the lowest order approximation for  $\bar{\Gamma}$ . We have from our previous work that

$$\begin{aligned} \beta^2\Gamma_{BB}^{(2)}(1) &= \text{Im}\mathcal{O}[R_-(1 + iE_1)^2] \\ &= -\rho_0^{-4} \int \frac{d\bar{\omega}_3}{2\pi} \frac{d\bar{\omega}_4}{2\pi} \frac{d^d\bar{k}_3}{(2\pi)^d} \frac{d^d\bar{k}_4}{(2\pi)^d} \delta(q + \bar{k}_3 + \bar{k}_4) \bar{G}_{\rho\rho}(\bar{k}_3, \bar{\omega}_3) \bar{G}_{\rho\rho}(\bar{k}_4, \bar{\omega}_4) \\ &\quad \times \text{Im}\mathcal{O}[R_-(1 + iE_1)^2]. \end{aligned}$$

In the nonergodic phase we have the  $\delta$ -function contribution

$$\bar{G}_{\rho\rho}(\bar{k}_3, \bar{\omega}_3) = -\rho_0\beta V(\bar{k}_3)F(\bar{k}_3)2\pi\delta(\bar{\omega}_3) \quad (233)$$

and we find immediately that we can set  $E_1 = 0$ , and

$$\text{Im}R_- = \pi\delta(\omega_1 + \omega_3 + \omega_4) = \pi\delta(\omega_1). \quad (234)$$

Comparing with Eq.(231),

$$\beta^2\bar{\Gamma}_B(q) = \frac{1}{2\rho_0^4} \int \frac{d^dk}{(2\pi)^d} \rho_0\beta V(k)F(k)\rho_0\beta V(q+k)F(q+k).$$

It is useful to write

$$F(q) = S(q)f(q) \quad (235)$$

and it is  $f(q)$  that is conventionally called the ergodicity parameter.



Using the same set of dimensionless variables as in the static calculations, the nonergodicity equation can be written in the conventional form

$$\frac{f(q)}{1 - f(q)} = w(q), \quad (236)$$

where

$$w(q) = \frac{\pi}{12\eta} \tilde{S}(q) \int \frac{d^d k}{(2\pi)^d} \tilde{V}(k) f(k) \tilde{S}(k) \tilde{V}(q+k) f(k+q) \tilde{S}(q+k). \quad (237)$$

Before solving Eq.(236) numerically, it is useful to obtain an approximate analytical solution. Notice that the combination  $\tilde{V}(k)\tilde{S}(k)$  (see Fig. 3) is sharply peaked at the structure factor maximum. Then, to a reasonable approximation, we can replace  $f(k)$  with its value at the maximum such that

$$w(q) = f^2(q_0) \tilde{S}(q) M(q) \quad (238)$$

with  $M(q)$  the same quantity that appears in the static calculation. Putting this result in the nonergodicity equation we obtain

$$\frac{f(q)}{1 - f(q)} = f^2(q_0) \tilde{w}(q), \quad (239)$$

where

$$\tilde{w}(q) = \tilde{S}(q) \tilde{M}(q) \quad (240)$$

is known from our static structural calculations. We now have a closed algebraic equation for  $f(q_0)$  if we set  $q = q_0$  in Eq.(239) with  $f_0 = f(q_0)$  and  $w_0 = \tilde{w}(q_0)$ :

$$\frac{f_0}{1 - f_0} = f_0^2 w_0. \quad (241)$$

Discarding the ergodic solution  $f_0 = 0$ , we have a quadratic equation to solve given by

$$w_0 f_0^2 - w_0 f_0 + 1 = 0 \quad (242)$$

with the solution

$$f_0 = \frac{1}{2} \left( 1 + \sqrt{1 - 4/w_0} \right). \quad (243)$$

Note that there is no transition for  $w_0 < 4$ . For  $w_0 > 4$ , we obtain the full wave number dependence by putting  $f_0$  back into

$$f(q) = \frac{\tilde{w} f_0^2}{1 + \tilde{w} f_0^2}. \quad (244)$$

It is easy to compute the  $w_0$  numerically using the Percus Yevick (PY) structure factor. In Fig. 4 we plot  $w_0$  versus  $\eta$ . We find that the ENE transition density, when  $w_0 = 4$ , is  $\eta^* = 0.53$ . The associated  $f(q)$  is shown in Fig. 5 for several densities in the nonergodic phase.

Returning to the full problem, Eq.(236) can be rewritten in the form

$$f(q) = \frac{w(q)}{1 + w(q)}. \quad (245)$$

The solution of this equation is available via direct iteration. If we use an initial trial value of  $f_0(q) = 1/2$  in Eq.(237), we generate an initial trial value  $w_0 = 0.25\tilde{S}(q)M(q)$  to obtain

$$f_1(q) = w_0/(1 + w_0). \quad (246)$$

We continue iterating via

$$f_{\ell+1}(q) = w_\ell/(1 + w_\ell) \quad (247)$$

and find that

$$\lim_{\ell \rightarrow \infty} (f_{\ell+1} - f_\ell) = 0. \quad (248)$$

For pure hard-sphere systems in three dimensions we find an ergodic-nonergodic transition at  $\eta^* = 0.76$ . Clearly this density is physically unattainable. It is interesting to solve Eq.(245) using the first order result  $\tilde{V} = \tilde{S}^{-1} - 1$  rather than the second order result. Despite the fact that there is small change in the effective potential in going from first to second order one finds a substantial change in the critical density from 0.76 to 0.60. Thus, we see that  $\eta^*$  is a sensitive quantity.

In Fig. 6 we plot  $f(q)$  for hard spheres for a set of  $\eta > \eta^*$ . We find a lot of structure in  $f(q)$ . Comparing the approximate  $f(q)$  given in Fig. 5 with the full numerical solution we see good agreement despite very different transition densities.

### XIII. CONCLUSIONS

We established here that the theory of time-dependent fluctuations in equilibrium can be organized around the fluctuation-dissipation theorem. Using the FDT one can relate the two-point response function to the two-point correlation function. In turn this gives

a linear-relation between self-energy components. We show more specifically the nontrivial result that the collective parts of the self-energies at second order satisfy a FDT. We find the second order self-energies as functionals of the physical density-density correlation functions. The role of the three-point vertex functions are crucial in this analysis.

Using the FDT the static structure is separated from the dynamical information and gives one a self-consistent expression for the static structure factor in terms of the potential. This expression can be recovered from a strictly static analysis. We show how the problem can be turned around and posed as in MCT. The structure factor is assumed to be given and we solve for the effective potential  $\tilde{V}$  that produces the known structure factor. At first order, the effective potential is proportional to the static direct correlation function. At second order,  $\tilde{V}$  is similar to the first order result except at small wavenumbers.

We also show that the theory is compatible with an ENE transition at second order. The critical density is sensitive to the details of the calculation. Using the Percus-Yevick approximation for hard spheres we find an ENE transition at the physically inaccessible density  $\eta^* = 0.76$ .

In a future work we will explore the role of the single-particle dynamics which occur in this theory. The treatment of these degrees of freedom gives one information about the equation of state,  $\langle \rho \rangle = \bar{\rho}(\rho_0, T)$ . The single-particle degrees of freedom contribute a second order contribution to the self-energies which depends on the full density-density correlation function.

Our focus here, because of its simplicity, has been on Smoluchowski dynamics, but as will be discussed elsewhere, the method developed here can be applied to Newtonian dynamics and Fokker-Planck dynamics as well as a broader class of models.

The approach presented here allows for a systematic method for analyzing corrections to this second order result including determination of higher order correlation functions. We plan to analyze the third order contribution to the collective self-energy soon.

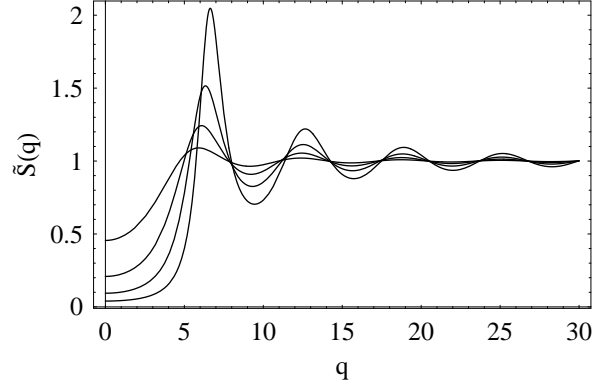
We guess that the theory presented here can be organized to give a theory of freezing. One can then do simultaneous free energy comparisons between the nonergodic state and the crystalline solid state.

### Acknowledgments

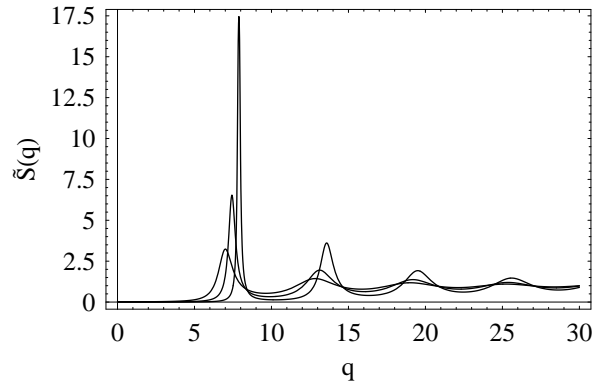
I thank the Physics Department and the Joint Theory Institute at the University of Chicago for support. A special thanks is due to M. Zannetti for showing that  $G_{\rho B}$  satisfies a simple linear fluctuation-dissipation theorem and for other comments on this work. I thank David McCowan for help with the figures and comments and I thank Paul Sprydis and S. Das for their comments on this work.

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  - <sup>12</sup> A brief discussion of the storied history of Brownian motion is given in Refs. 2 and 20 in FTSPD. We will refer to the noninteracting limit of Smoluchowski dynamics as the Brownian gas.

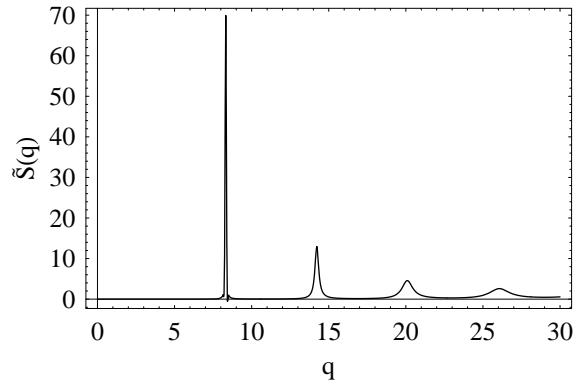
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- <sup>19</sup> The static Ornstein-Zernike relation that connects the radial distribution function to the direct correlation function.
- <sup>20</sup> In different contexts the kinetic kernels have different names. In the field theory context the kernels are typically called self-energies, in the kinetic theory case, where the analysis is in terms of retarded quantities, the kernel is called a memory function, and in the general case it can be called a dynamic direct correlation function.
- <sup>21</sup> Note that  $b_1$  depends on the  $n$   $t_i$  while the operator depends only on  $t_1$ .
- <sup>22</sup> G. F. Mazenko, D. D. McCowan and P. Spyridis, *in preparation*.
- <sup>23</sup> An advantage of working in equilibrium is that we can take the initial time to minus infinity. We called this the field-theory protocol in FTSPD.



(a)



(b)



(c)

FIG. 1: The static structure factor as determined using the Percus-Yevick Hard Sphere Approximation for (a)  $\eta = 0.1, 0.2, 0.3$ , and  $0.4$ , (b)  $\eta = 0.5, 0.6$  and  $0.7$ , and (c)  $\eta = 0.8$ . Larger first structure peak height corresponds to larger  $\eta$  within each plot.

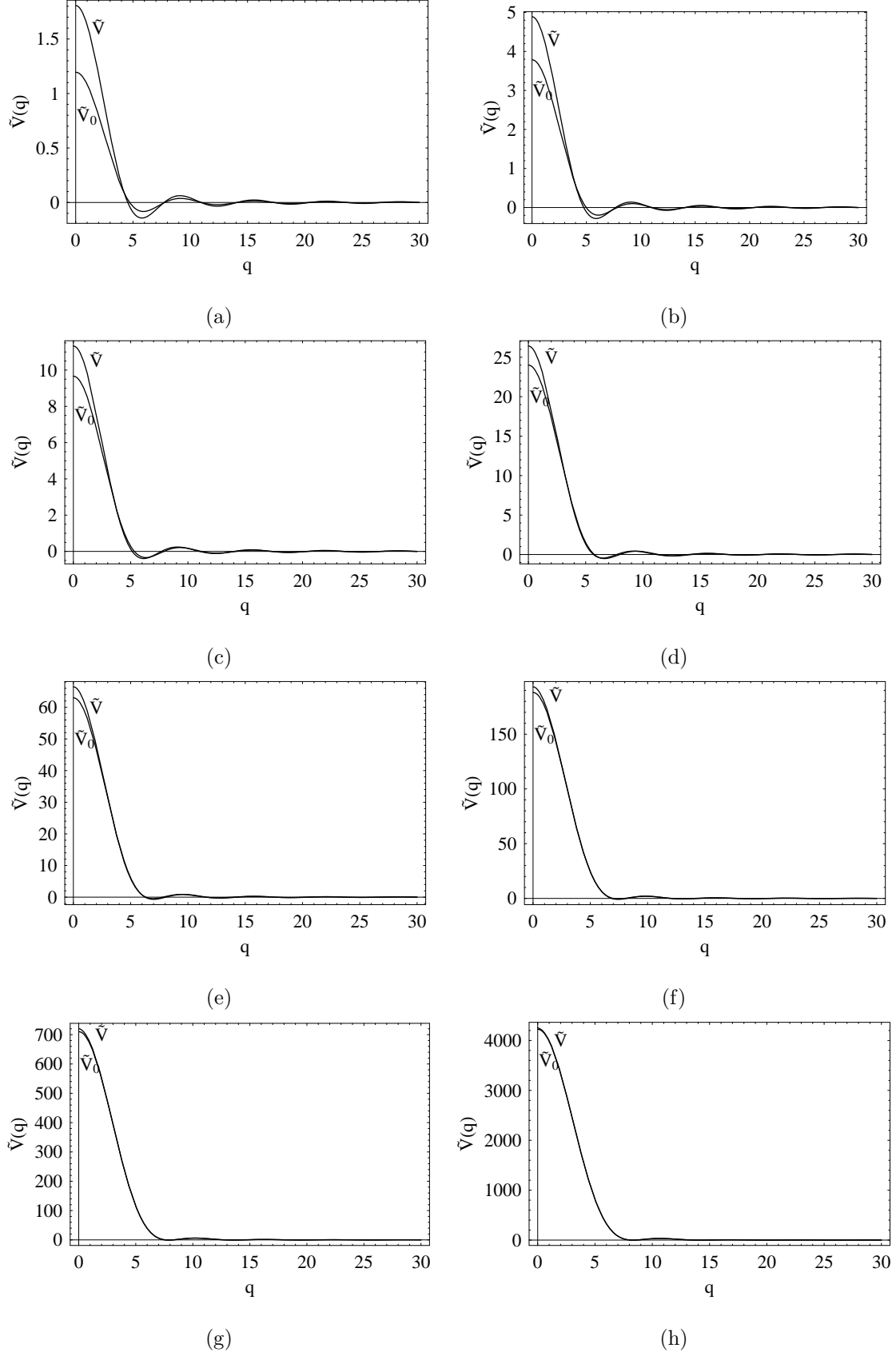


FIG. 2: The zeroth order potential  $\tilde{V}_0(q)$  and the numerical solution for the full potential  $\tilde{V}(q)$  from (a)  $\eta = 0.1$  to (h)  $\eta = 0.8$  in increments of 0.1.

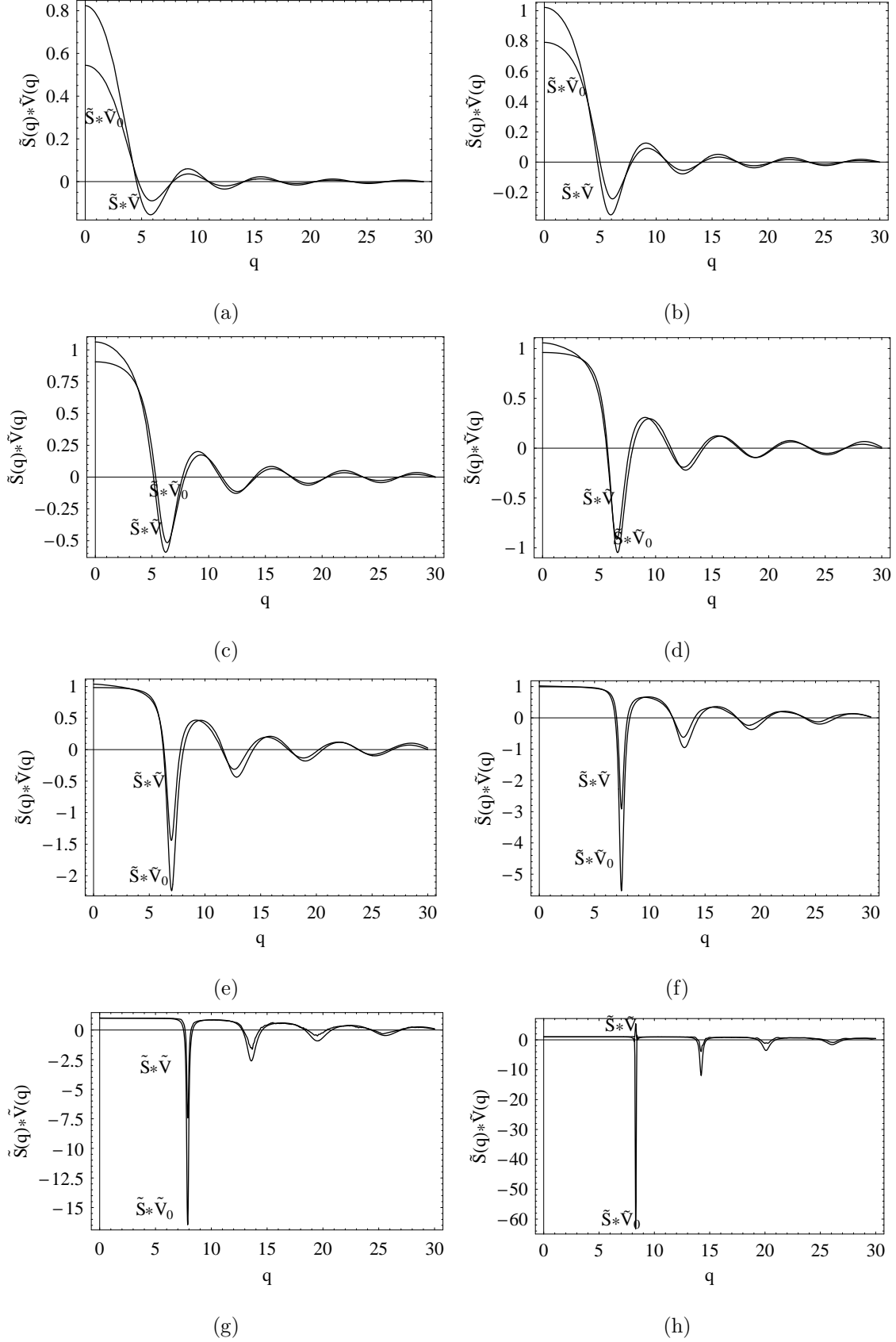


FIG. 3: The potential times the static structure factor for both  $\tilde{V}_0(q)$  and  $\tilde{V}(q)$  from (a)  $\eta = 0.1$  to (h)  $\eta = 0.8$  in increments of 0.1.



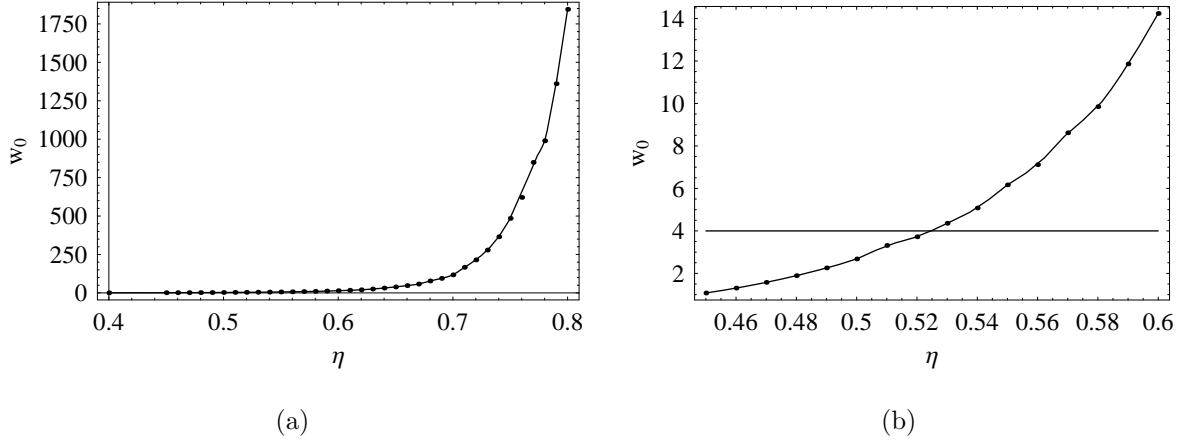


FIG. 4: Values of  $w_0$  versus  $\eta$ . Note that the line crosses  $w_0 = 4$  (and therefore enters the nonergodic regime) near  $\eta = 0.525$ . (The solid line is to guide the eye only.)

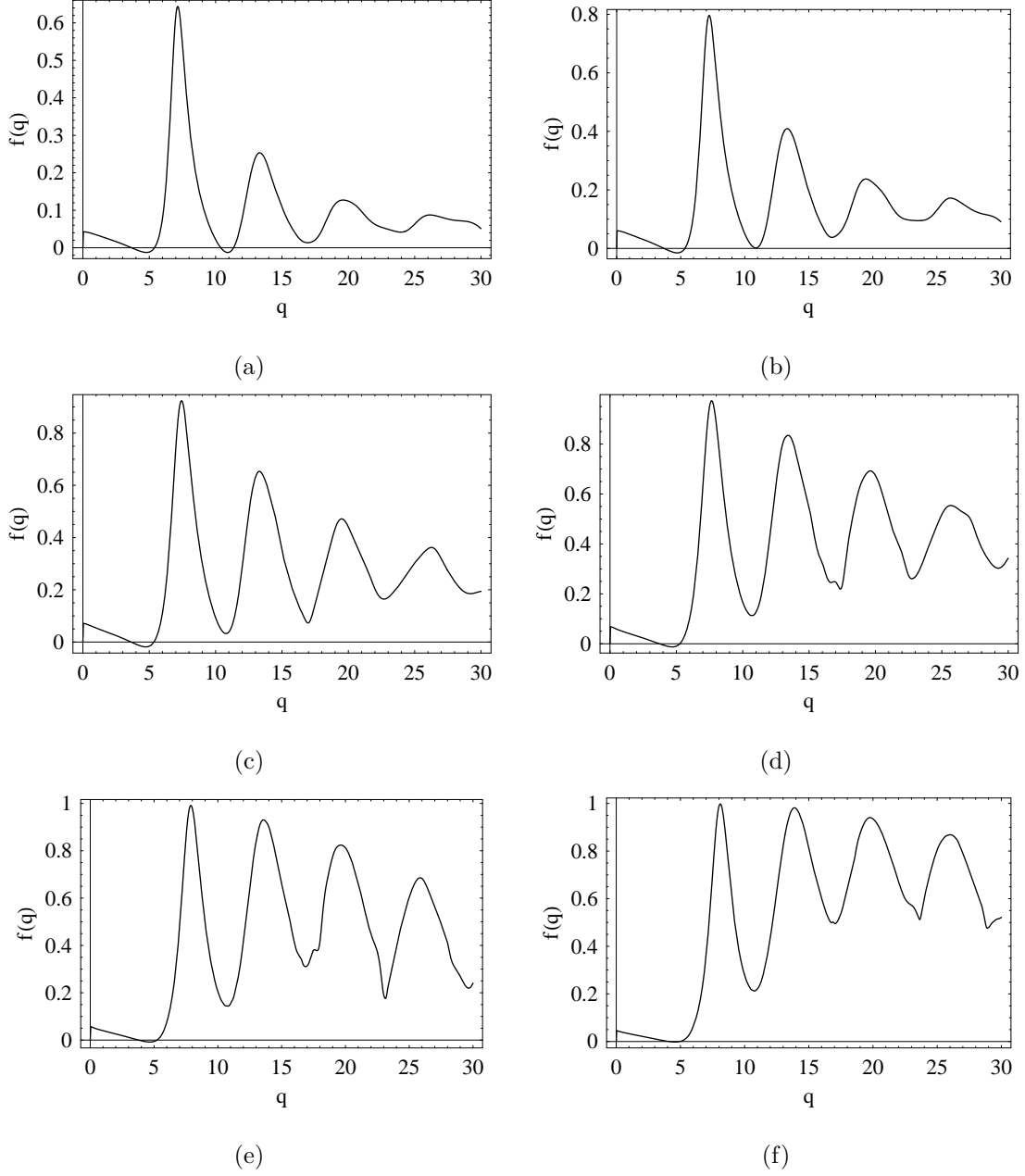


FIG. 5: Using the analytic approximation for  $f(q)$  given by Eq. (244), we plot the approximate form of the nonergodicity parameter for (a)  $\eta = 0.53$  (just above the analytic transition), (b)  $\eta = 0.55$ , (c)  $\eta = 0.60$ , (d)  $\eta = 0.65$ , (e)  $\eta = 0.70$  and (f)  $\eta = 0.75$ .

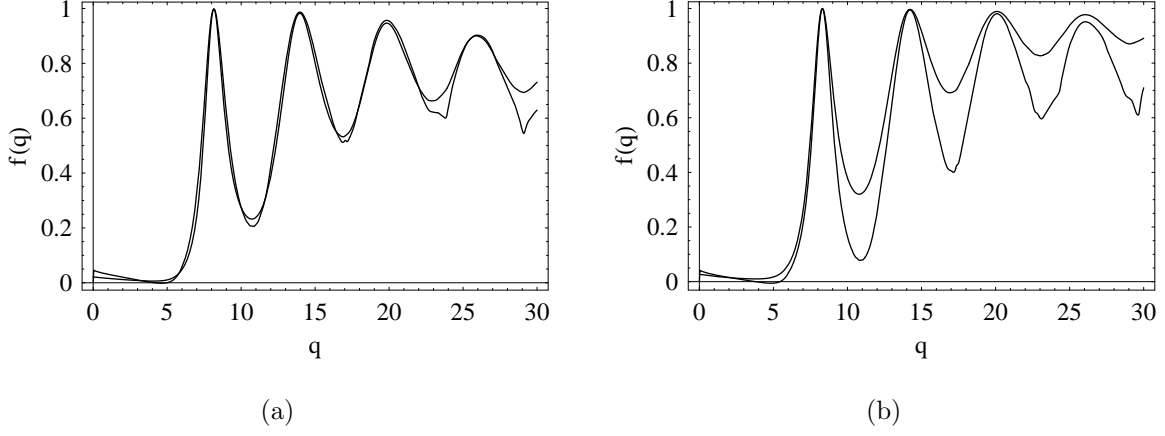


FIG. 6: Numerically, we find a transition at  $\eta = 0.763$ . We plot the numerical solution and the analytic solution for (a)  $\eta = 0.763$  and (b)  $\eta = 0.8$ . The more ragged and slightly lower line in each plot is the analytic approximation.